THE PROCEEDINGS OF
THE PHYSICAL SOCIETY

Section A

VOL. 62, PART 7 1 July 1949 No. 355 A

A Recording Spectrometer for Raman Spectroscopy

BY C. H. MILLER, D. A. LONG, L. A. WOODWARD
AND H. W. THOMPSON
Physical Chemistry Laboratory, Oxford

MS. received 10th January 1949

ABSTRACT. A description is given of a photoelectric recording spectrometer for Raman spectroscopy incorporating a high-intensity excitation system and a novel amplification device. Operation of the exciting mercury arc lamps from 50 c/s. mains imparts to the light signal, and consequently to the current from the photo-multiplier tube, a 100 c/s. periodicity. After amplification by a narrow band-pass amplifier, rectification is achieved in a push-pull phase-sensitive (homodyne) rectifier, by " mixing " the signal with a fixed voltage of identical periodicity. The rectified signal is fed through a filter to a cathode follower valve which provides the power to operate a recording milliammeter. This method of rectification, in conjunction with appropriate filter, effectively reduces the bandwidth of the amplifier, with consequent great improvement in the signal/noise ratio. With this arrangement cooling of the photo-multiplier is unnecessary for normal work. Using a spectrometer of small aperture and resolution and a Raman tube of 35 ml. capacity, traces of the Raman spectrum of carbon tetrachloride show no appreciable background noise.

§1. INTRODUCTION

THE difficulties involved in the accurate determination of the intensities of Raman lines by microphotometry from photographic plates are well known. The direct recording of Raman spectra using photoelectric cells has been achieved by Rank and his collaborators (Rank, Pfister and Coleman 1942, Rank, Pfister and Grimm 1943, Rank and Wiegand 1946) and also by Chien and Bender (1947). The present paper describes an instrument we have recently built for this purpose, using a different method of electronic amplification. Our results suggest that the electrical circuits which we have used possess definite advantages over those previously described, particularly as regards the attainment of high gain with low noise. The spectrometer hitherto available to us for this purpose falls far short in resolving power of that which would be justified by the performance of the electrical part of the instrument. In spite of this, excellent records have been obtained. Therefore, although it is hoped eventually to employ a better spectrometer, it seems desirable to describe the arrangement now, and on the basis of our results to indicate changes which may lead to further improvement.

§2. THE OPTICAL SYSTEM

Preliminary work showed that high-pressure mercury arcs such as Osira tubes were less satisfactory than Hanovia lamps, the latter having less continuous background and being free from "foreign" lines.

Two arrangements for exciting the Raman spectra have been used. In the first a horizontal Raman vessel, of the Wood's tube form with rear-blackened horn, was placed at one focus of an elliptical chromium-plated reflector. This tube, which was fitted with a jacket for water-cooling or for a filter solution, had a total volume of about 60 ml., of which only about 40 ml. were irradiated. A 500-watt cylindrical Hanovia lamp was placed at the other focus of the reflector, only about half its length being effective for the irradiation of the liquid under investigation. Adjusting devices were provided so that the Raman tube could be accurately aimed relative to the spectrometer collimator, and suitable stops were also used between the tube and the slit so that only light scattered by the liquid entered the spectrometer.

With this arrangement good records of the Raman spectrum of carbon tetrachloride were obtained, the background noise being inappreciable even though the photo-multiplier tube was not cooled below room temperature.

A considerable advantage was obtained, however, by adopting a more intense method of excitation based upon an arrangement due to Dr. A. C. Menzies. A vertical water-cooled Raman tube without horn (volume 35 ml.) is placed with two vertical 500-watt Hanovia mercury lamps inside a water-cooled enclosure. The inner surface of the enclosure is coated with magnesium oxide, which has a high reflectivity for the exciting light. The scattered light passes out through the lower plane end of the Raman tube and is reflected into the spectrometer through a condenser lens, whose focal length is chosen so as to ensure most efficient gathering of the light scattered by the liquid (see Nielsen 1930). The whole is carefully aimed so that only such light enters the spectrometer. With this arrangement the intensity of scattering is so great that the Stokes–Raman lines of carbon tetrachloride can be seen by placing the eye at the position of the photocell.

The spectrometer is a small Hilger constant-deviation glass monochromator in which both lenses are 3·15 cm. in diameter and 18·5 cm. focal length. The small prism gives relatively poor resolution: using slits 0·02 mm. wide it is not possible to separate lines less than about 20 cm^{-1} apart in the region of 4358 A. Also, in order to obviate curvature of the spectrum lines, short slits are used (only 0·35 cm. in height). These are severe limitations on the amount of light entering the spectrometer, and the fact that Raman lines can be recorded using lower gain than would give rise to a significant level of noise is highly satisfactory. The prism is caused to rotate by a synchro-motor and gear, so that the spectrum traverses the exit slit. In the region of 4358 A. the speed of scanning is about 0·1 A. per second.

The photo-multiplier tube (R.C.A. type 1.P.21) is placed behind the exit slit in a cylindrical housing having a glass window at the front, the whole being surrounded by a metal can into which solid carbon dioxide or a freezing mixture can be placed. The photo-multiplier tube is kept dry by closing the top of its housing by a cap sealed with Apiezon wax, and placing a little calcium chloride at the bottom of the housing. Small electrical heaters near the window and near the cap carrying the leads prevent condensation of moisture when the tube is cooled. The photo-multiplier is protected from stray light by suitable stops,

particularly between the exit slit of the spectrometer and the window. Although good records can be made without cooling, considerable reduction of noise can be achieved by surrounding the photo-multiplier tube with solid carbon dioxide.

§3. THE ELECTRICAL SYSTEM

The detection and recording of the Raman spectrum is carried out as follows. The mercury arc lamps are operated from the 50 c/s. mains supply and so produce a pulsating light signal of 100 c/s. periodicity. Thus the photo-multiplier gives a pulsating current of the same periodicity. The voltage developed by this signal across a 1 megohm wire-wound load resistor is increased by an amplifier tuned flat between about 95 and 105 c/s., so as to produce a voltage having a peak value S. This latter is fed into a phase-sensitive (homodyne) rectifier, which produces a D.C. output voltage proportional to the entrant signal. The operation of the rectifier is as follows. The signal S is fed into one side of the circuit in phase with a constant voltage B of identical periodicity obtained from the mains supply, producing a resultant $(B+S)$. Into the other side of the circuit the signal S is fed out of phase with the constant voltage B, producing a resultant $(B-S)$. The two resultants are then coupled in opposition, so that a final D.C. output voltage proportional to $2S$ is obtained. The latter is then fed through a resistance-capacity filter to a cathode follower valve which supplies the necessary power to drive the pen recorder, a Tinsley recording milliammeter.

The advantage of the homodyne compared with a conventional amplifier is that any entrant voltages due to noise or such extraneous causes, which are not identical in frequency with the 100 c/s. voltage B, will produce beat voltages which can be removed by the filter preceding the cathode follower tube. The tuning is therefore sharp, and the reduction of noise in the amplifier is determined by the effectiveness of the filter following the homodyne rectifier. This filter can easily be adjusted for various speeds of response. There is no need for the main amplifier preceding the rectifier to be sharply tuned to the 100 c/s. signal, although a reasonably narrow bandwidth is desirable in order to avoid overloading of the later stages of the amplifier by the noise. Further, no difficulties arise from any variation in the mains frequency since it will have an identical effect upon both signal and beat voltage B.

An alternative method of amplification would be to use a very high load resistor of, say, 10^{10} ohms for the photo-multiplier output, followed by an electrometer triode and one or two stages of D.C. amplification. Such a load resistor cannot in practice be wire-wound, however, and will act as a semiconductor at the frequencies concerned, and thus, when carrying the signal current, will have an inherent noise greater than the Johnson noise. Using a 10^6 ohm wire-wound load resistor as in the system now described, with amplification at 100 c/s. there should be no fluctuations in the load resistor other than Johnson noise. The resistor is also sufficiently high in value to be well above the equivalent noise resistance of the first valve in the amplifier.

The details of the amplifier are as follows.

(a) *Main amplifier* (Figure 1).

Current from the photo-multiplier is first fed through a screened cable to the wire-wound load resistor (1 megohm), and the voltage drop is applied through a condenser to the grid of the first valve V1 which is a triode connected for least

internal noise, and having its cathode earthed, so that there is minimum pick-up from the heater circuit. The anode load resistors of V1 and V2 are wire-wound so as to minimize noise. V2 is a conventional voltage amplifier stage stabilized by negative feedback and followed by the gain control S1. Stage V3 has feedback applied through the network F1, which results in the response of V3 being that of a high-pass filter with cut-off frequency at about 95 c/s. Additional negative feedback is provided by the non-bypass cathode resistor, so as to improve stability. Stage V4 is similar to V3 except that feedback through F2 leads to the frequency response of a low-pass filter with cut-off frequency about 105 c/s. V5 is an additional voltage amplifier stage preceded by the gain controls S2 and P1.

In order to eliminate interference and pick-up, extensive screening is used in the early stages. All earth connections are made to the cathode of V1, which is also connected to an external earth. The whole amplifier is placed in a screening box, and all cables to the power supply are screened. The box is mounted on rubber shock absorbers to eliminate microphony.

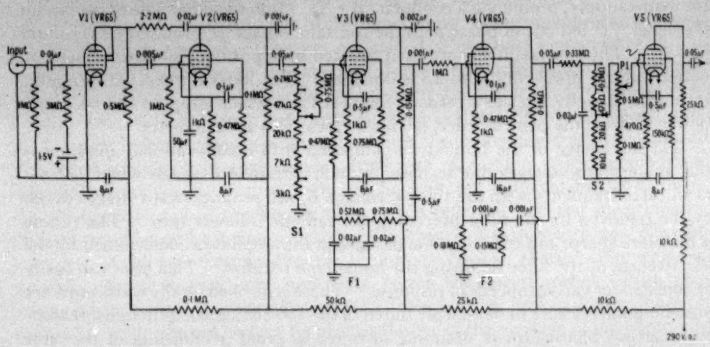


Figure 1.

(b) *Homodyne and output stages* (Figure 2).

In a normal rectifier noise voltages are rectified together with the signal voltage and produce their own fluctuating D.C. component in the output, this being superimposed upon the true D.C. signal. These noise fluctuations can be smoothed out, but their mean amplitude will remain as a residual D.C. voltage superimposed upon the signal. In the homodyne the mean value of such smoothed noise fluctuations is zero, so that the effect of filtering after rectification is similar to a narrowing of the bandwidth of the amplifier as a whole, in so far as reduction of noise is concerned.

In Figure 2 the valves V7 and V8 have the signal voltages fed in push-pull from the phase splitter V6 to their first set of control grids. The potentiometer P2 is preset for exact balance of V7 and V8. The 100 c/s. voltage for mixing with the signal is obtained by full-wave rectification of the mains in V10; and following the phase splitter V11, it is possible to vary the relative phase of the output by means of S4 and P3. Hence a synchronized voltage of variable phase is supplied to the second grids of V7 and V8 connected in parallel.

A smoothing filter of variable time-constant (S3A and S3B) is connected between the anodes of V7 and V8 and the control grids of the cathode follower V9, which drives the recorder. The potentiometer P4 controls the balance of the grids of V9 and acts as a zero-control. By means of S3A and S3B the effective bandwidth of the whole amplifier is variable in five steps.

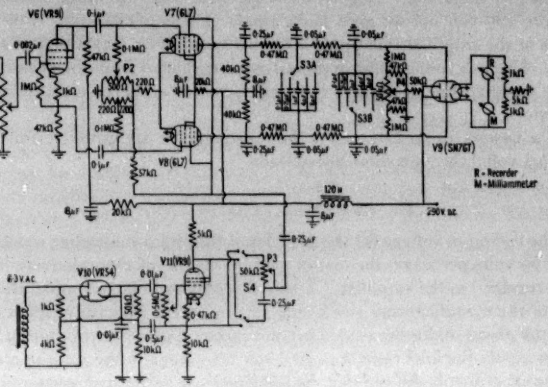


Figure 2.

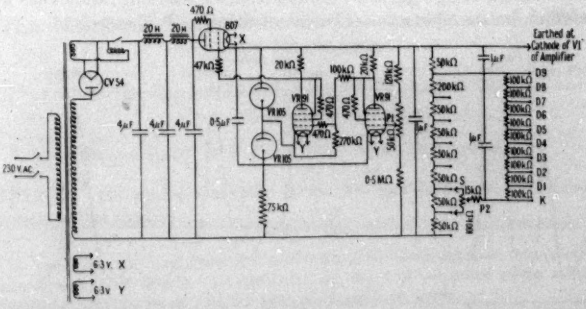


Figure 3.

(c) *Power supplies.*

The high voltage for the photo-multiplier dynodes is obtained from a smoothed power supply derived from the A.C. mains (Figure 3). A step-up transformer provides a voltage of about 1,000, which is then subjected to half-wave rectification and smoothing in the usual way. Regulation is achieved by means of degenerative feedback. Voltage variations in the output are applied to the grid of a VR91 tube and fed back through another VR91 to the grid of the regulator valve 807 in the correct phase, to offset changes in the output. The control grid resistor of the 807 valve is large in order to damp tendencies to oscillation. The potentiometer P1 is preset to determine the voltage at which the circuit regulates. This

final voltage is applied across a series of resistors and by means of the switch S and potentiometer P2 different total voltages can be taken off before final smoothing and division for the dynode stages. The ripple voltage is less than 0·002 volt, and total voltages between 400 and 800 (45 to 90 volts per stage) can be obtained.

The high voltage for the amplifier is provided by a regulator circuit similar to that just described. Regulation is excellent over the range 190 to 260 volts and the 290-volt output used has a ripple of about 0·03 volt. For the earlier stages of the amplifier this ripple is further reduced by smoothing to about 0·001 volt. All earth connections in this circuit are isolated from the chassis and made to the negative side of the H.T. line, which is earthed at the cathode of V1 in the amplifier.

The heaters for the cathodes in the main amplifier are supplied from accumulators (6·3 volts) through short heavy leads.

§ 4. GENERAL PERFORMANCE

The optimum voltage for the dynodes of the photo-multiplier was found to be about 66 volts per stage, the loss in gain by the use of this relatively low voltage being regained in the amplifier. Using this dynode voltage supply, the specifications of the manufacturers give a current gain in the photo-multiplier of 5×10^4. With the photo-multiplier cooled in solid carbon dioxide the minimum detectable voltage across the load resistor is 10^{-7} volt for a signal/noise ratio of about unity, and the experiments showed that the Johnson noise in the load resistor (1 megohm) is much less than this. Thus the input current to the amplifier is about 10^{-13} amp., the time-constant being sufficiently low to permit the scanning rate already quoted. The minimum detectable primary current is then 2×10^{-18} amp.

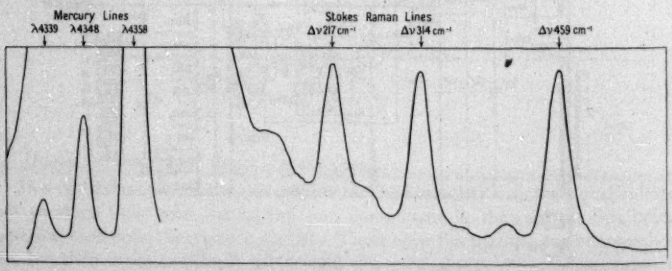


Figure 4.

Figure 4 shows part of a typical record of the Stokes–Raman spectrum of carbon tetrachloride obtained with the vertical Raman tube of 35 ml. capacity (see above). This record was taken with the photo-multiplier at room temperature and with an amplifier gain of only about one-fifth of the maximum practicable under these conditions. The performance indicates that a Raman tube of considerably smaller volume could be satisfactorily used with a spectrometer of greater resolution, particularly where wider slits might be possible.

Figure 4 also shows the exciting mercury line 4358 A. and its accompanying mercury lines 4348 and 4339 A., recorded with much lower amplification than that used for the Raman spectrum.

§5. FURTHER IMPROVEMENT OF THE SYSTEM

A number of improvements of the instrument are planned, and some have already been carried out. The lack of sharpness of the recorded lines in Figure 4 arises from the poor resolving power of the spectrometer. It is proposed to replace this by an instrument of greater aperture and resolution.

Another alteration is the use of a double recorder. When lines are so strong as to drive the first pen off the paper, the second pen, operated by a less sensitive ammeter, records them. Both the pens record on the same chart.

ACKNOWLEDGMENTS

We are indebted to Dr. A. C. Menzies for showing one of us a magnesium oxide-coated excitation arrangement similar to that described above. We also wish to express our thanks to the Hydrocarbon Research Group of the Institute of Petroleum for a grant covering part of the cost of the apparatus. One of us (D.A.L.) is indebted to the Department of Scientific and Industrial Research for a maintenance allowance, and another (C.H.M.) to the Rhodes Trustees for a scholarship, enabling them to take part in the work.

REFERENCES

CHIEN, J. Y., and BENDER, P., 1947, *J. Chem. Phys.*, **15**, 376.
NIELSEN, J. R., 1930, *J. Opt. Soc. Amer.*, **20**, 701.
RANK, D. H., PFISTER, R. J., and COLEMAN, P. D., 1942, *J. Opt. Soc. Amer.*, **32**, 390
RANK, D. H., PFISTER, R. J., and GRIMM, H. H., 1943, *J. Opt. Soc. Amer.*, **33**, 31.
RANK, D. H., and WIEGAND, R. V., 1946, *J. Opt. Soc. Amer.*, **36**, 325.

The Neutrons Emitted in the Disintegration of Lithium by Deuterons

BY L. L. GREEN AND W. M. GIBSON
Cavendish Laboratory, Cambridge

Communicated by O. R. Frisch ; MS. received 21st January 1949

ABSTRACT. The photographic plate method has been used in an investigation of the neutrons from the reaction

$$^{7}_{3}\mathrm{Li}+^{2}_{1}\mathrm{D}\rightarrow{}^{8}_{4}\mathrm{Be}+^{1}_{0}\mathrm{n}.$$

The results are in general agreement with those of Richards, but show the structure of the neutron groups more clearly. In particular, the shape of the broad group attributed by Richards to a level in ^{8}Be at $3{\cdot}0\pm0{\cdot}4$ MEV. is discussed in detail.

The total energy release is $15{\cdot}0\pm0{\cdot}15$ MEV., and evidence is put forward for the existence of energy levels in ^{8}Be at 2·8 MEV., 4·05 MEV., 4·9 MEV., and 7·5 MEV.

§1. INTRODUCTION

THE neutrons from the reaction

$$^{7}_{3}\mathrm{Li}+^{2}_{1}\mathrm{D}\rightarrow{}^{8}_{4}\mathrm{Be}+^{1}_{0}\mathrm{n}$$

have been studied by Richards (1941). He used the photographic plate technique to obtain the energy distribution of the neutrons emitted at right angles to the direction of the incident deuteron beam. He obtained evidence for a group at 14 MEV., corresponding to the formation of ^{8}Be in its ground state, as well as evidence for a broad level in ^{8}Be at 3 MEV. and another at 7·5 MEV.

This reaction is of considerable interest, mainly because of the information which it can give about energy levels in ^{8}Be. There is much evidence available about these levels, and Wheeler (1941) has discussed the subject theoretically on the assumption that the ^{8}Be nucleus can be considered made up of two separate α-particles comparatively loosely bound together. The neutrons themselves are useful for experiments in which energies up to 15 MeV. are required.

The application of the photographic plate technique to the study of neutron spectra has been described by Powell (1940, 1943) and Richards (1941). Since then the accuracy of the method has been increased by the introduction of concentrated emulsions (Demers 1946, Powell, Occhialini, Livesey and Chilton 1946); the use of Ilford concentrated emulsions for the investigation of the neutrons from the reaction

$$^{14}_{7}\mathrm{N} + ^{2}_{1}\mathrm{D} \rightarrow ^{15}_{8}\mathrm{O} + ^{1}_{0}\mathrm{n}$$

has been described by Gibson and Livesey (1948). The technique of "temperature development", outlined by Dilworth, Occhialini and Payne (1948), now makes it possible to develop uniformly emulsions of thickness 300 μ or more. With 300 μ emulsions there is a greater chance that a long proton track will remain within the layer, and they are therefore more satisfactory than 100 μ emulsions for the investigation of neutron spectra which extend to energies much above 5 MeV.

In view of these improvements in the photographic plate technique, it was thought that a further study of the Li + D neutron spectrum would be profitable.

§ 2. EXPERIMENTAL TECHNIQUE

Ilford C.2 Nuclear Research plates, with emulsion thicknesses ranging from 100 μ to 300 μ, were exposed to the neutrons emitted from a thick lithium hydroxide target. The target was bombarded by a deuteron beam of mean energy 930 kev. from the Cavendish Laboratory 1 MV. set, an average irradiation lasting for 45 minutes with a deuteron beam of 80 microamperes. The plates were held in two positions at a distance of 17 cm. from the target; one set was arranged to receive, at glancing incidence, the neutrons leaving the target at an angle of 120° with respect to the direction of the deuteron beam ("120° neutrons"), while the other set of plates received the neutrons leaving the target at 0° ("0° neutrons").

The plates with 100 μ emulsions were developed in the usual way, by soaking for 45 minutes in I.D.19 developer diluted to 1 in 10. Thicker emulsions were processed by the method outlined by Dilworth, Occhialini and Payne (1948): the plates are first soaked in water at 5° C. for 30 minutes, and then in equally cold developer (I.D.19 diluted to 1 in 5) for 90 minutes. This impregnates the emulsion with developer while allowing little actual development to take place. The main development occurs when the plates are immersed for 30 minutes in developer at 18° C., and is uniform throughout the depth of the emulsion. Development is arrested by immersion of the plates in a stop-bath at 5° C.

§ 3. MEASUREMENTS

The plates were examined on a microscope built specially for nuclear research by Cooke, Troughton and Simms, with two different combinations of objectives and eyepieces which gave overall magnifications of 750 and 1,225. Measurements

of the length, the angle of dip, and the horizontal direction were made for each proton track which started within a definite area of the emulsion; the energy of the neutron responsible for the track was calculated by the method described by Gibson and Livesey (1948).

First, 1,000 tracks were measured in 100 μ emulsions exposed to the 0° neutrons, and a similar number for the 120° neutrons. Only tracks of protons recoiling forwards at angles of less than 19·5° from the direction of the neutron were accepted. Tracks corresponding to neutrons of energy less than 4·5 MeV. were also neglected, as it was expected that many of these would be due to the reactions

$$^{2}_{1}\mathrm{D} + ^{2}_{1}\mathrm{D} \rightarrow ^{3}_{2}\mathrm{He} + ^{1}_{0}\mathrm{n} + 3{\cdot}23 \text{ MeV.}$$

$$^{6}_{3}\mathrm{Li} + ^{2}_{1}\mathrm{D} \rightarrow ^{7}_{4}\mathrm{Be} + ^{1}_{0}\mathrm{n} + 3{\cdot}4 \text{ MeV.}$$

In the 120° plates an extra 230 tracks corresponding to neutrons of over 7·5 MeV. were measured.

In 300 μ emulsions 480 tracks were measured for 120° neutrons and 300 for 0° neutrons; the lower limits of neutron energy were 6 MeV. and 7 MeV. respectively, and the upper limit of scattering angle was reduced to 9·5°. As changes in angle of dip due to collisions caused appreciable inaccuracies in the measured lengths, the angle of dip was measured at intervals of 100 μ along the projected length of each track, instead of just at the beginning; the total length was then obtained by calculating the actual length in space of each section of the track and adding the results.

§4. NEUTRON SPECTRA

For each set of measurements the number of observed tracks was tabulated as a function of the calculated neutron energy, which for this purpose was taken to the nearest 0·1 MeV. In order to reduce the effects of statistical fluctuations, the numbers were later regrouped at 0·3 MeV. energy intervals.

To obtain from the observed spectra correct distributions of the numbers of neutrons, it was necessary to multiply the number of tracks corresponding to each neutron energy by a factor proportional to the neutron–proton scattering cross-section at this energy (Sleator 1947) and inversely proportional to the fraction of such tracks which would be expected not to escape from the surfaces of the emulsion; this fraction depends on the neutron energy, the emulsion thickness, and the maximum scattering angle for which tracks are recorded; it was obtained from the equation given by Gibson and Livesey (1948), except at energies above 7·5 MeV. in the 100 μ emulsions, where the equation had to be replaced by arithmetical and graphical approximations. The low statistical accuracy of our results at the higher energies did not justify a detailed investigation of the bending of tracks and its effect on the escape correction. The arbitrary constant in the multiplying factor was chosen so as to make the latter equal to unity for a neutron energy of 11 MeV.

Figures 1 to 6 show the final results of the observations. Each ordinate is proportional to the number of neutrons in an energy interval of 0·3 MeV., and in the region of 11 MeV. is equal to the actual number of proton tracks observed in such an interval. The standard deviation of each point is indicated by a vertical line.

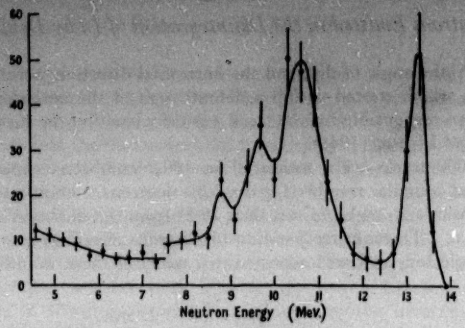


Figure 1. 120° neutron spectrum, from measurements in 100 μ emulsions.

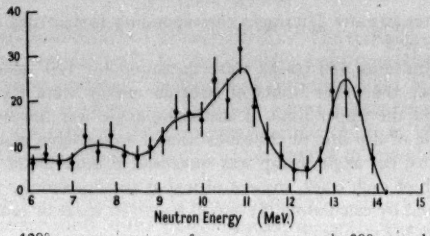


Figure 2. 120° neutron spectrum, from measurements in 300 μ emulsions.

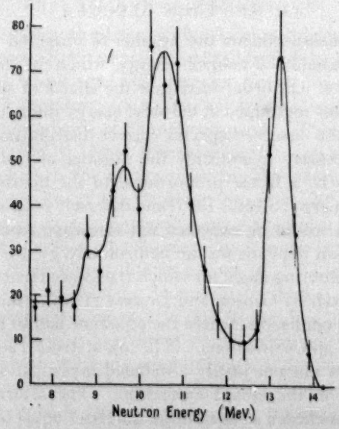


Figure 3. 120° neutron spectrum, from all measurements combined.

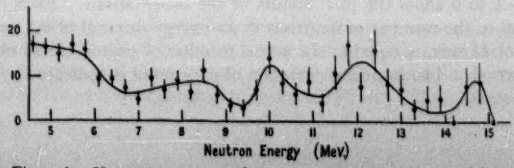


Figure 4. 0° neutron spectrum, from measurements in 100 μ emulsions.

Figure 1 is the spectrum obtained from the 1,230 tracks measured in 100 μ emulsions exposed to the 120° neutrons. There is a discontinuity at 7·5 MeV., as tracks corresponding to lower energies were neglected during part of the observations. Figure 2 shows the results of measurements of tracks in the 300 μ emulsions exposed to the same neutrons, and Figure 3 shows the combined results of all measurements on tracks due to 120° neutrons of energy greater than 7·5 MeV.

Figure 4 represents the spectrum of the 0° neutrons, between 4·5 MeV. and 15MeV., obtained from 1,000 tracks measured in 100 μ emulsions. Figure 5 shows the results of measurements in 300 μ emulsions, the lower limit of energy being 7 MeV., and Figure 6 gives the complete results for 0° neutrons of energies greater than 7 MeV.

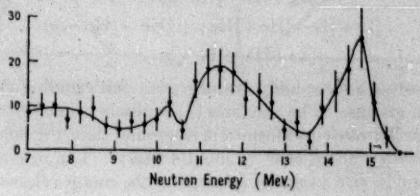


Figure 5. 0° neutron spectrum, from measurements in 300 μ emulsions.

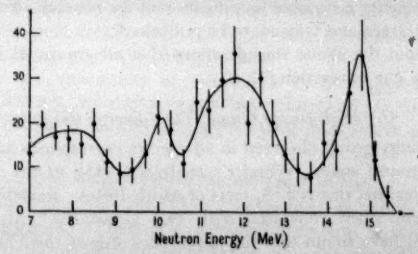


Figure 6. 0° neutron spectrum, from all measurements combined.

(*Note.*—In Figures 1 to 6, and Figure 9, each ordinate is proportional to the number of neutrons in an energy interval of 0·3 MeV., and in the region of 11 MeV. is equal to the actual number of proton tracks observed in such an interval.)

Considering first the 120° results, we find a sharp peak at 13·3 MeV. in each spectrum. There is also, extending from 9 MeV. to 11·5 MeV., a very broad group which appears to be composed of a main peak at 10·6 MeV. and a subsidiary peak at 9·65 MeV. There is a continuous distribution down to 4·5 MeV., showing a marked increase at the lower energies. In the results for the 300 μ emulsions there are indications of a possible peak between 7 and 8 MeV., but this group does not show up in the 190 μ emulsion results. There is, on the other hand, an indication of a peak at 8·8 MeV. in the 100 μ results which does not appear in the 300 μ spectrum.

The results for the 0° neutrons have not the same statistical accuracy as those for the 120° neutrons since, although the number of tracks measured was nearly as large, it was spread over a wider energy range. However, the results show similar features: in all spectra there is a high-energy group with a peak at about 14·8 MeV., and again there is a broad group at a lower energy. In this case it extends from 10·8 MeV. to 13·0 MeV. A fairly well

defined group with a peak at 10·15 MeV. appears in the results for both 100 μ and 300 μ emulsions, and there are indications of a broad group between 7·0 MeV. and 8·6 MeV. This is superimposed on the continuous background which again extends down to 4·5 MeV. with greater intensity at the lower energies.

§ 5. DISCUSSION OF RESULTS

(i) *Possible Reactions*

The neutrons emitted by lithium under deuteron bombardment may be due to the reactions:

$$^{7}_{3}\mathrm{Li} + ^{2}_{1}\mathrm{D} \rightarrow ^{8}_{4}\mathrm{Be} + ^{1}_{0}\mathrm{n}, \quad \ldots\ldots(1)$$

$$^{7}_{3}\mathrm{Li} + ^{2}_{1}\mathrm{D} \rightarrow ^{4}_{2}\mathrm{He} + ^{4}_{2}\mathrm{He} + ^{1}_{0}\mathrm{n}, \quad \ldots\ldots(2)$$

$$^{7}_{3}\mathrm{Li} + ^{2}_{1}\mathrm{D} \rightarrow ^{4}_{2}\mathrm{He} + ^{5}_{2}\mathrm{He}; \quad ^{5}_{2}\mathrm{He} \rightarrow ^{4}_{2}\mathrm{He} + ^{1}_{0}\mathrm{n}, \quad \ldots\ldots(3)$$

$$^{6}_{3}\mathrm{Li} + ^{2}_{1}\mathrm{D} \rightarrow ^{7}_{4}\mathrm{Be} + ^{1}_{0}\mathrm{n}. \quad \ldots\ldots(4)$$

Reaction (2) involves a three-body disintegration and cannot give rise to homogeneous neutron groups. The reactions (3) similarly cannot give homogeneous groups, and if the $^{5}_{2}$He nucleus is formed in its ground state, the maximum possible energy of a neutron emitted at 0° is about 4·8 MeV. The masses (Bethe 1947) of $^{6}_{3}$Li, $^{2}_{1}$D, $^{7}_{4}$Be and $^{1}_{0}$n give a value of 3·4 MeV. for the energy release in reaction (4), which cannot therefore give neutrons of energy greater than 4·5 MeV., the lower limit of measurement; a separate investigation of the neutrons from this reaction has been made (Green and Gibson, to be published).

It follows from the above considerations that all groups of neutrons above 4·5 MeV. must be due to reaction (1).

(ii) *High-energy Group, Total Energy Release*

The high-energy group observed in all spectra corresponds to the formation of ^{8}Be in the ground state. Wheeler's analysis (1941), of the results of Laaf and Fink indicates that this is a $^{1}S_{0}$ level of width 100 ev., unstable to the extent of about 125 kev. when compared with two α-particles. Also Walker and McDaniel (1948) have found that the observed width of the 17 MeV. γ-ray line produced by bombarding lithium with protons is consistent with the existence of a similar sharp level in ^{8}Be. The observed widths of our groups, whose shapes are shown in detail in Figures 7 and 8, should therefore be determined entirely by the thick-target and range-straggling effects.

The straggling of proton ranges in concentrated emulsions is known (Lattes, Fowler and Cuer 1947) to be about 0·3 MeV. at these energies. The effect of the thickness of the target was obtained from the excitation function measured by Bennett, Bonner, Richards and Watt (1947) and the equation

$$8{\cdot}008\,Q = 9{\cdot}017\,E_{\mathrm{N}} - 2\sqrt{(2{\cdot}033\,E_{\mathrm{D}}E_{\mathrm{N}})}\cos\theta - 5{\cdot}993\,E_{\mathrm{D}}.$$

This equation follows from the kinematics of the reaction, and connects the neutron energy E_{N} with the deuteron energy E_{D} for particular values of Q and of the angle of emission θ. The excitation function was used to give the yield expected from the deuterons which had been slowed down to a particular energy E_{D} in the target, and the equation to give the energy of the resulting neutrons.

The width of the group in the 120° spectrum should be about 0·4 MeV. This is mainly due to straggling, since at this angle E_{N} does not vary much with E_{D}. The term "width" is used here and throughout this paper to mean the interval between the two energies for which the intensity is half that at the peak. The

observed width is 0·6 MeV. and the peak is at 13·22 MeV.; this gives a Q-value of 15·0 ± 0·1 MeV.

The thick-target effect causes greater broadening in the corresponding group of 0° neutrons. The width for half-intensity should be 0·7 MeV., but there will

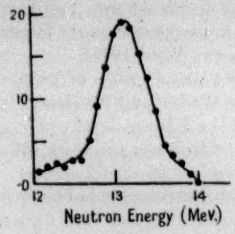


Figure 7.
Shape of high-energy group in 120° spectrum.

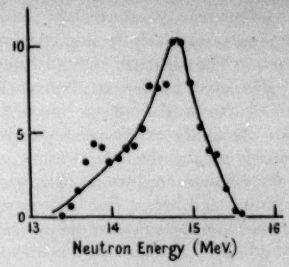


Figure 8.
Shape of high-energy group in 0° spectrum.

(*Note.*—Ordinates in Figures 7 and 8 are proportional to the numbers of neutrons in energy intervals of 0·1 MeV., smoothed by adding to each the mean of its neighbours.)

also be a tail on the low-energy side which may extend as far as 1·3 MeV. below the peak. The experimental width is 0·8 MeV. and the maximum intensity is at 14·8 MeV.; this again gives $Q = 15·0 \pm 0·1$ MeV.

Allowing for the uncertainty of ± 0·08 MeV. in the range–energy relation between 13 and 15 MeV., we may give as a final value $Q = 15·0 \pm 0·15$ MeV. This agrees well with the value of 15·04 MeV. given by the mass values quoted by Bethe (1947).

(iii) *Other Groups, Excited Levels in* ^{8}*Be.*

The broad group occurring about 3 MeV. below the high-energy group requires more careful discussion. There is a considerable amount of evidence on levels occurring in ^{8}Be in the neighbourhood of 3 MeV. above the ground state. Wheeler (1941) shows that the main results of experiments on α–α scattering are accounted for by an excited state of zero angular momentum and energy 2·8 MeV. Dee and Gilbert (1936) have attributed the continuum in the α-particle energy distribution observed in the reaction ^{11}B(pα)^{8}Be to an excited state of width 0·8 MeV. and energy 3·0 MeV. A re-examination of these results by Bethe (1937) indicated that a level at 2·8 MeV. and width 0·8 MeV. was consistent with the observations. Smith and Murrell (1939) attributed a group of α-particles from the reaction ^{10}B(dα)^{8}Be to the formation of ^{8}Be in a level at 3 MeV.

Wheeler identifies the 2·8 MeV. α–α scattering level with the first vibrational state on the two-α-particle model, and it is reasonable to identify this with the 3 MeV. level observed in the boron disintegrations.

Bonner, Evans, Malich and Risser (1948) have reported that the energy distribution of the α-particles associated with the β-disintegration of ^{8}Li may be explained by the assumption of a level in ^{8}Be at 3·4 ± 0·4 MeV., with $J = 2$, and a further broad level at 7–9 MeV.

Recently, Walker and McDaniel (1948) have confirmed the long-suspected existence of a 14·8 MeV. γ-ray from the reaction ^{7}Li(pγ)^{8}Be, as well as the well-known 17·6 MeV. γ-ray. The latter corresponds to the formation of ^{8}Be in its

ground state and the former to an excitation of 2·8 MeV. This level is probably the same as that observed in boron reactions and in α–α scattering, but the γ-ray line is found to have a breadth of about 2·1 MeV. instead of 0·8 MeV. This might indicate the presence of two unresolved lines.

Richards (1941), in an investigation of the reaction ^{7}Li(dn)^{8}Be, observed a very broad neutron group which he considered to be composed of two unresolved groups, due respectively to the 2·8 MeV. level of width 0·8 MeV. and to a level at 4·9 MeV. The existence of this 4·9 MeV. level was suggested by the observation of a 4·9 MeV. γ-ray by Bennett, Bonner, Richards and Watt (1941).

Our results clearly indicate the presence of a broad group of width about 2·0 MeV. As in the results of Richards and of Walker and McDaniel, this is considerably greater than the 0·8 MeV. width of the 2·8 MeV. level. The group due to the 4·9 MeV. level would be at too low an energy to account for the width of our group, and has in fact been separately resolved in the 0° spectra. The main group itself appears to be complex and is probably composed of two partially resolved groups. For convenience the spectra shown in Figures 3 and 6 are shown again in Figure 9, with the neutron energy scale replaced by a scale of the corresponding ^{8}Be excitation energy.

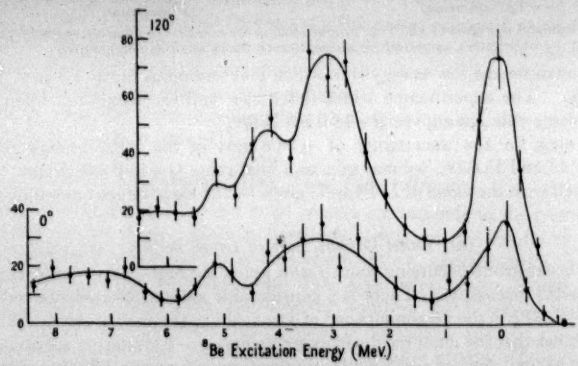


Figure 9. Neutron spectra, from Figures 3 and 6, plotted against ^{8}Be excitation energy.

The 120° spectra consistently show a partially resolved group at a neutron energy of 9·65 MeV. The main group has a maximum at 10·6 MeV., corresponding to a Q-value of 11·9 MeV. and an excited state in ^{8}Be at 3·0 MeV. The experimental width of this group is approximately 1·4 MeV.; when allowance has been made for straggling and the thick-target effect, this would indicate a width of approximately 0·8 MeV. for the 3·0 MeV. level.

The subsidiary peak at 9·65 MeV. corresponds to a Q-value of 10·85 MeV., and would require a level at 4·05 MeV. in the ^{8}Be nucleus. We cannot draw any conclusions about the width of this level, as the group is only partially resolved. An excited state at 4·05 MeV. would be consistent with the results of Walker and McDaniel, and of Richards; it may also be noted that Bonner, Evans, Malich and Risser (1948) have interpreted their results for the energy distribution of the α-particles from the β-decay of ^{8}Li by assuming a level in ^{8}Be at $3{\cdot}4 \pm 0{\cdot}4$ MeV.

The corresponding group in the 0° spectra may be complex, but the peak due to the 4·05 MeV. level is not resolved. The width of the group is 2·0 MeV., which

is greater than the value of 1·6 MEV. which the straggling and thick-target effects would give with a 3·0 MEV. level of width 0·8 MEV.

There is a well-defined peak in these spectra at 10·15 MEV., corresponding to a Q-value of 10·0 MEV. and requiring a level in ^{8}Be at 5·0 MEV. Smith and Murrell (1939) observed a group of α-particles from the reaction $^{10}B(d\alpha)^8Be$ which would have required an excited state of ^{8}Be at 4·8 MEV.; this group could, however, have been attributed to contamination of their target with lithium. It has already been mentioned that Bennett, Bonner, Richards and Watt (1941) have observed the emission of a 4·9 MEV. γ-ray from lithium bombarded with deuterons. This γ-ray was attributed to a level in ^{8}Be at 4·9 MEV., which was assumed to have odd angular momentum or odd parity or both, so that the ordinary break-up into two α-particles was forbidden. It is reasonable to ascribe our group of neutrons to the same level. There are also indications of the presence of a corresponding group of neutrons in the 120° spectra; the lower intensity in this direction may be connected with the odd angular momentum of the state.

The 0° spectra indicate the presence of a broad group of neutrons with a mean energy of 7·9 MEV. and width about 2·0 MEV. This would require a level in ^{8}Be at 7·4 MEV. and 2·0 MEV. wide. Richards has observed a neutron group in the 90° direction requiring a level at 7·5 MEV., approximately 1·7 MEV. wide. There are indications of a greater neutron intensity between 6·5 MEV. and 8·5 MEV. in our 120° spectra, but this group is not statistically significant.

In both the 0° and 120° spectra the continuous background of neutrons shows a pronounced increase at the lower energies. This may be another neutron group due, for instance, to the broad level at 10·0 MEV. suggested by Richards, or it may be a genuine rise in the intensity of the neutrons due to the reaction

$$^7_3\mathrm{Li} + {}^2_1\mathrm{D} \rightarrow {}^4_2\mathrm{He} + {}^4_2\mathrm{He} + {}^1_0\mathrm{n}.$$

ACKNOWLEDGMENTS

The authors wish to express their thanks to Professor O. R. Frisch and Dr. W. E. Burcham for advice and assistance, and to the Department of Scientific and Industrial Research for financial support.

REFERENCES

BENNETT, W. E., BONNER, T. W., RICHARDS, H. T., and WATT, B. E., 1941, *Phys. Rev.*, **59**, 904; 1947, *Ibid.*, **71**, 11.

BETHE, H., 1937, *Rev. Mod. Phys.*, **9**, 217; 1947, *Elementary Nuclear Theory* (New York: John Wiley & Son), p. 124.

BONNER, T. W., EVANS, J. E., MALICH, C. W., and RISSER, J. R., 1948, *Phys. Rev.*, **73**, 885.

DEE, P. I., and GILBERT, C. W., 1936, *Proc. Roy. Soc.* A, **154**, 279.

DEMERS, P., 1946, *Phys. Rev.*, **70**, 86.

DILWORTH, C. C., OCCHIALINI, G. P. S., and PAYNE, R. M., 1948, *Nature, Lond.*, **162**, 102.

GIBSON, W. M., and LIVESEY, D. L., 1948, *Proc. Phys. Soc.*, **60**, 523.

GREEN, L. L., and GIBSON, W. M., 1949, to be published.

LATTES, C. M. G., FOWLER, P. H., and CUER, P., 1947, *Proc. Phys. Soc.*, **59**, 883.

POWELL, C. F., 1940, *Nature, Lond.*, **145**, 155; 1943, *Proc. Roy. Soc.* A, **181**, 344.

POWELL, C. F., OCCHIALINI, G. P. S., LIVESEY, D. L., and CHILTON, L. V., 1946, *J. Sci. Instrum.*, **23**, 102.

RICHARDS, H. T., 1941, *Phys. Rev.*, **59**, 796.

SLEATOR, W., 1947, *Phys. Rev.*, **72**, 207.

SMITH, C. L., and MURRELL, E. B. M., 1939, *Proc. Camb. Phil. Soc.*, **35**, 298.

WALKER, R. L., and MCDANIEL, B. D., 1948, *Phys. Rev.*, **74**, 315.

WHEELER, J. A., 1941, *Phys. Rev.*, **59**, 27.

The Basis of the Electron Theory of Metals, with Special Reference to the Transition Metals

By N. F. MOTT
H. H. Wills Physical Laboratory, University of Bristol

MS. received 25th April 1949

ABSTRACT. It is shown that the collective electron and London–Heitler models are not to be regarded as different approximations to the same exact wave function for solids in which, according to the former model, there is a partially filled zone of energy levels. It can thus be shown why nickel oxide in the pure state is a non-conductor, although it contains an incomplete zone. The properties of the metals nickel, palladium and platinum are discussed in the light of these results ; platinum differs from nickel in that the orbital contribution to the moment of the elementary magnets is not quenched. A discussion is given of X-ray absorption edges, and it is shown why exciton lines are absent for metals.

§ 1. THE COLLECTIVE ELECTRON AND LONDON-HEITLER METHODS

In discussing the cohesive forces in metals, or their electrical or magnetic properties, it is first necessary to set up an approximate electronic wave function. In doing this, all investigators have used one or other of two approximations; these are:

(*a*) The London–Heitler or Heisenberg approximation, in which one starts from atomic wave functions, such as that in which $\psi_a(\mathbf{r}_n)$ describes the space coordinate of the nth electron in the atom a. One then forms products of the type

$$\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)\ldots,$$

multiplied by appropriate spin functions, and from these an anti-symmetrical determinant or sum of anti-symmetrical determinants can be set up. This method, though convenient for insulators such as NaCl, where each atom or ion is in a singlet state, has not been applied with much success to metals, owing to the mathematical difficulties introduced by the spin degeneracy. The only exact result deduced by this method is that of Bloch (1930), who treated the case where the exchange integral between neighbours is positive, so that in the lowest state all spins are parallel (ferromagnetism); he showed that if I, I_0 are the values of the intrinsic magnetic intensity at temperatures T and zero,

$$I - I_0 = \text{const. } T^{3/2}. \qquad \ldots\ldots(1)$$

The same argument shows that the electronic specific heat with this model varies as $T^{3/2}$. The case where the exchange integral is negative is much more difficult and has not been used to obtain successfully the electronic specific heat. For a discussion of the paramagnetism in this case, cf. Hulthén (1936).

(*b*) The collective electron treatment, also first used in a quantitative way by Bloch (1928). This is the same as the molecular orbital method of quantum chemistry. Wilson (1931) first showed how convenient the model was for explaining the sharp division of pure solids at low temperatures into metals and non-conductors; the former are those with a partially filled "zone" of electronic states, the latter those in which all zones are either quite full or quite empty.

Stoner * has recently applied the model to ferromagnetics, and obtained a form for $I_0 - I$ which, though surprisingly similar to the $T^{3/2}$ law mentioned above, is derived in quite a different way. The experimental results are certainly not good enough to decide between them.

The main purpose of this paper is to suggest that these two models are *not*, as is usually believed, different approximations to the same exact wave function. We believe, on the other hand, that crystalline solids, which in model (*b*) have incomplete zones, fall quite sharply into two clases: those for which model (*b*) is a good approximation (metals), and those for which model (*a*) is a good approximation.

Let us consider first the physical properties of a substance which we believe to belong to the class (*a*), namely NiO. This has the simple cubic structure, and may be thought of as being made up of nickel ions Ni^{++} and oxygen ions O^{--}. It is paramagnetic (Batnagar and Bal 1934), the nickel ions being the paramagnetic elements. The nickel ion has the electronic configuration $(3d)^8$; the 3d state should give rise to a zone containing 10 electrons which may be split by a cubic field into sub-zones containing 4 and 6; thus, using model (*b*), at least one of these sub-zones is partly empty. Thus, according to model (*b*), NiO should show metallic conductivity, increasing as the temperature is lowered. But this is not in accordance with the facts. Pure nickel oxide is an insulator, and is transparent to visible light, being pale greenish yellow. And this is what we should expect, starting from model (*a*). In order that NiO should conduct, there must be present some Ni^{+++} ions and some Ni^{+} ions, which can move about by electron transfer. But a definite amount of energy, E say, is required to remove an electron from one ion (leaving Ni^{+++}) and to put it on a *distant* ion, forming Ni^{+}. Therefore, unless the crystal of NiO as a whole is in an excited electronic state (e.g. at a high temperature), no such pairs are present. Nickel oxide can actually be made to behave as a semiconductor by introducing Ni^{+++} ions into the lattice, e.g. by replacing some of the nickel ions by Li^{+} ions, an electron being removed from another ion to secure electrical neutrality (Verwey, Haayman and Romeyn 1948); clearly, then, electrons are not impeded by the rather large interionic distance (*c.* 7 A.) from jumping from ion to ion.

It has, of course, been noticed by many authors (e.g. Schubin and Wonsowski 1934) that the London–Heitler approximation does not allow for any electric current, and it has been suggested that, in the exact wave function, there will be present *ionized* states—i.e. some atoms having one extra electron and an equal number having one missing; these we may call positive holes. We suggest that this is not quite correct, and that, starting from the London–Heitler approximation, there will either be no pairs (electrons and holes) which have separated *many* atomic distances, or else, as one goes to higher approximations, the number of completely separated pairs will increase indefinitely, so that the whole approximation breaks down and one has to start with the collective electron treatment.

The evidence for this view is as follows:

(i) The facts about NiO quoted above and similar facts about oxides of other transition metals.

(ii) The difficulty in believing that a state with a *small* number of pairs can ever have lower energy than a state with no pairs. One will always have to do work to separate the electron and hole constituting the first pair to be formed,

* In a series of papers; for references cf. Stoner (1948).

because the electron and positive hole attract each other with a force derived from a potential energy $-e^2/\kappa r$, where κ is a dielectric constant. It is known from Schrödinger's equation that two particles which attract each other with a force of this type are capable of existing in a number of stationary states in which they are bound to each other. On the other hand, if some pairs already exist, it no longer follows that work must necessarily be done to form some more. This is because the material is now in a state where a current can be carried; therefore (Mott and Jones 1936, p. 87), the field between the electron and hole is now screened, and is of the form to be derived from a potential $-(e^2/\kappa r)\exp(-qr)$. The constant q increases with the number of electrons and holes present. In a field of this sort, if q is large enough, there are no bound stationary states. It no longer follows, then, that work must be done when the number of pairs is increased; it is possible that energy may be gained, owing to the negative energy of particles with collective electron orbitals.

We suggest tentatively, then, that the energy E of a crystalline array of N atoms—e.g. an array of Na atoms or Ni^{++} ions, may be as shown in Figure 1. E is here the energy corresponding to a wave function containing n pairs of electrons and holes and is plotted against n. E may be supposed to be the minimum (and hence most accurate) energy value obtainable from a wave function of London–Heitler type with ionized states. E, as we have shown, will always rise first as n increases. We suggest that it will then decrease. It may or may not drop below

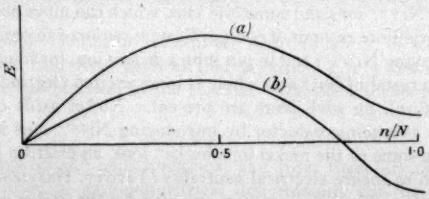


Figure 1. Hypothetical plot of energy E against number n of pairs, (*a*) for large separations between atoms as in NiO, (*b*) for small separations as in metals.

the value for $n=0$. Presumably it will not if the interatomic distance is large (case of NiO), but will otherwise (case of metals). If it does, the number of holes becomes large (comparable with N), the approximation breaks down, and we go over to the collective electron treatment.

Some further evidence that the view is correct may perhaps be provided by a recent theoretical paper on the wave functions of the hydrogen molecule (Coulson and Fischer 1949). These authors write the wave function in the unsymmetrical form

$$\{\psi_a(1)+\lambda\psi_b(2)\}\{\psi_b(1)+\lambda\psi_a(2)\},$$

where ψ_a, ψ_b are atomic wave functions for electrons in the atoms a, b, and λ is a parameter. By minimizing the energy calculated with this wave function, λ is determined as a function of the distance R between the nuclei of the two atoms. In H_2 this is actually 1·4 A.; the calculations show that $\lambda=1$ gives the best approximation up to $R=2{\cdot}3$ A., but thereafter λ tends rapidly to zero. In our view the abrupt transition only occurs for infinite chains or lattices.

On the view explained above, therefore, if a substance such as NiO were subjected to very high pressure it should suddenly show metallic conduction for some value of the pressure, and the effective number of free electrons would suddenly jump to about one per atom. This view seems to be in accord with the observed fact that no metals show a very small effective number of free electrons except bismuth and similar elements (Mott and Jones 1936, p. 210). We believe that at the absolute zero of temperature a very small number of free electrons free to take part in a current is impossible, because the electrons and holes would attract each other and form bound pairs, i.e. electrons trapped in the field of holes. A metal substance is only a conductor at $T=0$ if there are enough electrons and holes to screen the field round any one of them sufficiently to prevent pair formation. Bismuth, of course, proves the rule because, although the number of free electrons is very small, their effective mass is also very small (Mott and Jones 1936, Chap. VI), and hence much less screening (smaller q) is necessary to prevent pair formation.

Experiments on the conductivity of cupric salts would be of great interest. One cannot say *a priori* whether or not they should show metallic conduction. According to Hilsch and Brunner (1947), CuS is a superconductor.

§ 2. THE TRANSITION METALS Ni, Pd AND Pt

Turning now to a metal such as nickel, we see that it can be represented as follows. Suppose that a London–Heitler type of wave function were set up representing nickel atoms in the singlet state $(3d)^{10}$; if *a few* electrons are removed and put into the 4s conduction band, leaving mobile holes in the 3d band, the energy will at first rise. But it seems very plausible that it will fall again, as in Figure 1, as the number is increased, owing to the bonding effect of the 4s conduction electrons—described of course by wave functions of the collective electron type. All the experimental evidence from the magnetic properties of these metals and their alloys goes to show that a minimum in the energy is reached when 0·6 holes per atom have been formed, giving 0·6 conduction electrons.

We thus consider that nickel contains 0·6 conduction electrons described by periodic wave functions and 0·6 holes; these must also be described by periodic wave functions extending through the lattice, quite independently of how big the interatomic distance may be. This is because the number of holes is non-integral; one could not set up a London–Heitler wave function with no ionized states for this case, and it seems certain that these holes can move through the lattice and contribute to a current. The model is essentially the same as the overlapping band model first introduced by Mott (1935), though we would now stress the applicability of the collective electron treatment for the holes rather than for the electrons of the d band.

The large electronic specific heats shown by Ni, Pd and Pt at liquid helium temperatures is known to be due to the holes, which can be treated in the usual way as a degenerate gas of particles with large effective mass. It is at first sight surprising that these metals do not all show an electronic specific heat at high temperatures given by

$$(C_v)_{el}=0{\cdot}6\times\tfrac{3}{2}R=1{\cdot}8\,\text{cal/gm. atom.}$$

For nickel the position is complicated by the transition at the Curie point, though some 30° above it the effect dies out and the specific heat seems in good agreement with theory (Wohlfarth 1949); but Pd and Pt certainly do not show so large a term. For Pd a careful analysis has been given by Clusius and Schachinger

(1947), showing at 1,000° K. an electronic term of about 0·9 cal/gm. atom. The probable reason is the form of the d band, shown by Jones and Mott (1937) for small overlap between the wave functions to be as seen in Figure 2 (see also Slater 1936); the calculations of Jones and Mott were for a simple cubic lattice). If, as is quite possible, the d zone in Pd is full up to near the top of the first maximum,

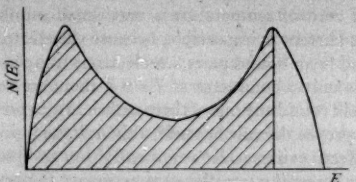


Figure 2. Plot of $N(E)$ as a function of E for a d band.

it is clear that the specific heat of the holes will not tend to the classical value but to a lower one. Calculations of the electronic specific heat with various band forms could easily be carried out and would be of interest. The reason for the difference between Ni and Pd is not known.

It has been suggested (Mott and Jones 1936, p. 222, Pauling 1949) that the magnetic carriers in nickel are not single holes, as stated here, but double holes, that is to say, ions in the triplet state of configuration $(3d)^8$. This suggestion was made in order to account for the paramagnetic behaviour of nickel above the Curie point, the slope of the line ($1/\chi$ versus T) agreeing with the hypothesis that the elementary magnets have $j=1$ instead of $j=\frac{1}{2}$, g of course remaining equal to 2. But it is clear now that this hypothesis is inadmissible, because coupled spins would obey Einstein–Bose rather than Fermi–Dirac statistics, and thus would give an electronic specific heat proportional to $T^{3/2}$ instead of the observed T. Wohlfarth (1949) has shown that the observed paramagnetic behaviour can be explained in terms of the collective electron treatment without making any assumptions about coupled spins; one would have to go to higher temperatures than are actually possible to obtain a true paramagnetic magneton number.

In nickel, of course, the g-value for the holes is 2, there being no orbital contribution. Probably this is not the case for platinum, the orbital motion and spin remaining coupled to give $j=5/2$ and $g=6/5$; spectroscopic data for the free atom shows that the interval between the terms of the spin doublet of the ion in the state $5d^9$ is of the order 1 ev. for Pt, while the corresponding interval for Ni is 0·25 ev. There is no difficulty whatever in describing mathematically, through periodic wave functions of the collective electron type, the motion through the lattice of the configuration $5d^9$ with coupled spin and orbit.

The strongest evidence that in metallic platinum the spin–orbit coupling is not broken down comes from the measurements of Cauchois and Manescu (1940) and Coster and de Lang (1949) on the L absorption edges of the x-ray spectra. For the L_1 edge one neither expects, nor finds, any sharp line at the edge due to transitions into the empty d states, because the initial L state is s. For L_2 and L_3, on the other hand, the initial state is p. For the free atom the empty state in the 5d shell has the j value 5/2; one would therefore expect a transition from L_3 ($j=3/2$) but not from L_2 ($j=1/2$). This is in fact what one finds in the

metal, showing that the spin–orbit coupling is not broken down. If it were broken down, the empty d states in the metal would be a mixture of the atomic states with $j=3/2$ and $j=5/2$, and both edges would give lines of comparable strength at the edge. If it is possible to observe the lines for nickel, they should appear both for the L_2 and L_3 absorption edges.

A further application of these ideas to x-ray absorption spectra may be made. One expects that the x-ray absorption edge of an insulator will consist of a series of lines, more or less broadened by lattice vibrations, leading up to a series limit. This is because the ejection of an electron from an inner shell leaves behind a positive charge; there is thus in the insulator a field of potential $-e^2/\kappa r$, and for the excited electron a series of stationary states must exist in this field *below* the conduction band. If κ is large, these states will be close together and difficult to observe; they seem however to have been observed in manganate ions (Sunner 1941) for the K absorption edge of manganese.

In metals no such "exciton" lines have been observed. The reason seems to us to be the following: the field round the positive charge left when the electron is ejected is screened, and of the form $-(e^2/r)\exp(-qr)$. Now if q were not big enough to prevent the formation of bound states in this field, then, according to the argument given above, the atoms from which an electron is missing and those with an extra electron would join together to form pairs, and the material could no longer be a conductor.

Turning now to Bloch's law (1) for I_0-I in ferromagnetics, we see that the original derivation is valid only for non-conducting materials (e.g. ferrites). Döring (1949) has, however, shown that for low temperatures it can be derived more generally, from the assumption that the energy E of a small volume containing a large number of elementary magnets depends on the three components of magnetization I_x, I_y, I_z through a formula of the type

$$E=A[(\text{grad}\, I_x)^2+(\text{grad}\, I_y)^2+(\text{grad}\, I_z)^2],$$

giving its local dependence on the direction of magnetization. The derivation does not, therefore, depend on the use of one model or the other. Thus the $T^{3/2}$ must be regarded as correct at low temperatures, regardless of any special model; it is analogous to the Debye T^3 law for the specific heat. Stoner's treatment is analogous rather to the Einstein treatment, and should be a good approximation only for higher temperatures, where the "spin waves" have short wavelength.

For non-conducting paramagnetics we have no theoretical or experimental information about the electronic specific heat as T tends to zero. A theoretical treatment, owing to the difficulty of handling the spin degeneracy, has not been given (cf. Bethe 1931).

REFERENCES

Batnagar, S. S., and Bal, G. S., 1934, *J. Ind. Chem. Soc.*, **11**, 603.

Bethe, H., 1931, *Z. Phys.*, **71**, 205.

Bloch, F., 1928, *Z. Phys.*, **52**, 553; 1930, *Ibid.*, **61**, 206.

Cauchois, Y., and Manescu, I., 1940, *C.R. Acad. Sci., Paris*, **211**, 172.

Clusius, K., and Schachinger, L., 1947, *Z. Naturforschung*, **2a**, 90.

Coster, D., and de Lang, H., 1949, *Physica*, in the press.

Coulson, C. A., and Fischer, I., 1949, *Phil. Mag.*, **40**, 386.

Döring, W., 1949, *Z. Phys.*, in the press.

Hilsch, R., and Brunner, H., 1947, quoted by E. Justi, *Leitfähigkeit und Leitungsmechanismus fester Stoffe* (Göttingen, 1948).

HULTHÉN, L., 1936, *Proc. Amst. Acad.*, **39**, 190.
JONES, H., and MOTT, N. F., 1937, *Proc. Roy. Soc.* A, **162**, 49.
MOTT, N. F., 1935, *Proc. Phys. Soc.*, **47**, 571.
MOTT, N. F., and JONES, H., 1936, *Theory of the Properties of Metals and Alloys* (Oxford : Clarendon Press).
PAULING, L., 1949, *Report of Paris Conference on Chemical Bonds.*
SCHUBIN, S., and WONSOWSKI, S., 1934, *Proc. Roy. Soc.* A, **145**, 159.
SLATER, J. C., 1936, *Phys. Rev.*, **49**, 537.
STONER, E. C., 1948, *Rep. Prog. Phys.*, **11**, 43 (London : Physical Society).
SUNNER, V. H., 1941, *Thesis*, Upsala.
VERWEY, E. J. W., HAAYMAN, P. W., and ROMEYN, F. C., 1948, *Chemisch. Weekblad*, **44**, 705.
WILSON, A. H., 1931, *Proc. Roy. Soc.* A, **133**, 458.
WOHLFARTH, E. P., 1949, *Proc. Roy. Soc.* A, **195**, 434.

The Experimental Basis of Electromagnetism—Part III: The Magnetic Field

BY N. R. CAMPBELL AND L. HARTSHORN

MS. received 3rd March 1949

ABSTRACT. The principles outlined in previous parts, published in the *Proceedings of the Physical Society* in 1946 and 1948 respectively, which dealt with the direct current circuit and with electrostatics, are here applied to magnetism, with the object of showing how the basic concepts are defined in terms of the operations actually performed in measuring them. This part is confined to a discussion of the vector **B**, which is shown to be measurable independently of a knowledge of any other magnitude. It is solenoidal, and can therefore be determined at all points, even those within solid bodies.

§1. INTRODUCTION

THE general purpose of this work, as stated in the abstract of Part I (Campbell and Hartshorn 1946) *, was "to show to what extent the working principles of electromagnetism can be soundly based on real experimental facts, as distinct from the imaginary experiments which are common to most expositions of the subject". The general principles by which magnitudes are established in terms of experimental operations were described in §2 of that paper, and at the outset we were optimistic enough to believe that by systematically applying these principles to operations that would be generally admitted as established practice, we should be able to derive the working laws of the experimentalist and a coherent outline of the whole subject in a form free from "mathematical fictions", that is to say, concepts like point charges that are so remote from real experiment that they must be classed as auxiliary devices invented by the human mind rather than anything encountered in nature.

We had some success in treating in this way the direct current circuit (Part I, 1946) and electrostatics (Part II, 1948), though it must be confessed that in Part II the jump from experiment to general law was not always so obvious as to leave no doubt in the mind of the reader about the wisdom of dispensing with the auxiliary devices. We have in the present part applied the same treatment to magnetism, and we have to admit that our early optimism has not been altogether justified. The laws that we have been able to base directly on real experiments can scarcely be regarded as forming a coherent structure, and it therefore seems

* For references seen end of Part IV, p. 000.

likely that theoretical magnitudes having no direct reference to real experiment form a necessary part of the subject as it is practised today. But though the magnitudes that arise directly from real experiments may not be sufficient, it is at least important that we shall know which they are, and their precise significance in terms of the operations that we actually perform. This part is therefore devoted to a consideration of the most characteristic experimental methods employed in the investigation of magnetic materials and of the magnitudes and laws which arise directly from them. These, in our view, constitute the experimental basis of the subject.

§ 2. THE FLUXMETER

In accordance with our general principles, our first step must be to seek among the instruments used in modern magnetic measurements one whose operations define a magnitude that can be measured independently of any other magnitude. Such an instrument is to be found in the fluxmeter. At first sight it may seem surprising that so complicated an instrument should be accepted as fundamental. The principle is, however, very similar to that which leads us to accept operations performed with balances and clocks, which are quite as complicated as fluxmeters, as the basis of our ideas of mass and time.

By a fluxmeter we mean the familiar combination of a search coil and ballistic galvanometer, the coil having its terminals close together, and being connected to the galvanometer, which is direction-sensitive, by long, flexible, twisted or concentric leads. (The term fluxmeter is often confined to an instrument in which the ballistic galvanometer is of a special kind, but we think it less objectionable to extend this meaning somewhat than to coin a new term.) If the search coil, after having been at rest for a long time in the neighbourhood of a magnet, is moved suddenly relative to it and is then brought to rest again, the galvanometer gives a characteristic response in the form of a transient deflection passing through one or more maximum values. We shall apply the term magnet to any system that produces such responses, so that it includes, not only permanent magnets and electromagnets in the conventional sense, but also current circuits not associated with any magnetic material. Similar responses can be produced by changes in the magnet, and in particular by changes in the current in a circuit forming part of the magnet without any relative motion of coil and magnet. The laws we are about to state in this section are true by whichever method the response is produced: it is convenient therefore to use terms that are equally applicable to either. We shall use the term "the system" to denote the whole combination of search coil, leads, galvanometer and magnet; and the "state of the system", that complex of conditions, sudden * change in any one of which may produce a response. Thus a change in the state of the system may include a change in the size or shape of the search coil, a displacement of the coil relative to the magnet, or a change in the state of the magnet, such as a change of current in a stationary coil or the displacement of a piece of magnetic material relative to neighbouring circuits.

So long as the changes of the state of the system are always sufficiently sudden and the galvanometer always starts from the same zero, such a system obeys two qualitative laws: (*a*) If two responses agree in one feature, e.g. the first maximum,

* By terms such as "sudden", "close together", "long time", we mean *so* sudden, *so* close, *so* long, etc., that the statements in which the terms are used are true. The fact involved in any such statement is that it can be made true by making the motion sudden *enough*, or by placing the terminals close *enough*, and so on. In this, of course, we are only following the practice of many other writers.

they agree in all; accordingly, each response can be completely characterized by a single parameter, say this first maximum. (*b*) The response is determined wholly by the terminal states between which the change occurs; it is unaffected by the intermediate states traversed in the passage from one terminal state to the other and by the period occupied by the traverse, so long as it is short enough. The system is therefore characterized by pairs of states for which an unambiguous definition of equality can be given, namely that one pair of states is equal to another pair when a change between one pair produces the same response as the change between the other. If we can associate a definition of addition with this definition of equality, we shall arrive at a magnitude, say A_{xy}, characteristic of the pair of states, (x, y), and measurable independently of the measurement of any other magnitude, and which thus resembles direct current, direct voltage, resistance and capacitance, which are fundamental in the discussions of the previous Parts.

Let us adopt then, as the definition of addition,

$$A_{xz} = A_{xy} + A_{yz}, \qquad \ldots\ldots (2.1)$$

or, in words, the value of A to be associated with a change of state from x to z is the sum of the values to be associated with the changes from x to y and from y to z, where y is any third state, not necessarily intermediate between x and z. (It is just worth noting that (2.1) is *not* a consequence of the law that A_{xz} is determined only by the terminal states; for a change from x to y that halts at z long enough to observe, the deflection is not "sudden".) We can now calibrate the scale of the galvanometer for A_{xy} by the standard procedure for independently measurable magnitudes. We choose arbitrarily some pair of states (a, b), and assign to A_{ab} the value unity. We find by experiment other states $c, d, e \ldots$ such that, according to the definition of equality,

$$A_{ab} = A_{bc} = A_{cd} = A_{de}. \qquad \ldots\ldots (2.2)$$

Then, according to the definition of addition, the numerals 2, 3, 4 . . . must be assigned to A_{ac}, A_{ad}, A_{ae} etc. Tests must now be applied to establish that the rules of arithmetic are obeyed consistently; thus we must enquire whether in fact A_{bd}, A_{ce}, ... are all 2 (i.e. that changes of state from b to d, from c to e . . . . all give the value 2 on the calibrated scale), that A_{be} is 3, and so on. Since $A_{xx} = 0$ (i.e. no change produces no deflection), we must have from (2.1) $A_{yx} = -A_{xy}$, and one of our tests must be to ascertain whether this is so. The necessity for this test is one reason why it was specified that the ballistic galvanometer should be direction-sensitive; of course it is not necessary that it should be such that the calibrated scale turns out to be symmetrical about the zero. A_{xy} in this general form, and without the limitations that will be imposed on it in the following sections, is not an important magnitude. It has no recognized name or symbol; no instrument is ever calibrated to read A_{xy} by this independent method, and no systematic tests are usually made to establish that (2.1) is actually true for fluxmeters calibrated in other ways. But it would be as wrong to dismiss as unimportant the fact that any satisfactory fluxmeter could be so calibrated as it would be to dismiss similarly the corresponding fact about D.C. ammeters, which also are never in practice calibrated by addition. The reasons are the same in both cases. The laws in virtue of which fluxmeters could be calibrated independently are often assumed to be true in using measurements made by fluxmeters calibrated in other ways; if a fluxmeter calibrated by some conventional method failed to

obey those laws, then that calibration would have to be judged wrong and "an explanation" would be sought in some defect of the method or the instrument; the independent method provides a criterion whereby all other methods can be judged.

§3. FLAT SEARCH COILS: B_n AND B

We shall now proceed to derive from this magnitude A_{xy} characteristics of pairs of states of a system including a magnet and a fluxmeter, first a magnitude X_x characteristic of a single state of the system, magnet and search coil, and then a magnitude B dependent only on the state of the magnet and position relative to it.

Change of the ballistic galvanometer or of the leads (if they provide any appreciable part of the resistance of the fluxmeter circuit) will change the deflection associated with any given change of the state of the system; but if the same change of state is always taken as the unit, and the scale calibrated in terms of that unit, then the value to be associated with any given change of state is independent of both the ballistic galvanometer and the leads; that is an experimental fact. If it were similarly independent of the search coil, A_{xy} would depend only on the state of the magnet and of the positions of the search coil relative to it; but the mention of "position" shows at once that complete independence of the search coil is impossible. For the position of the search coil relative to the magnet, which enters into the definition of the unit of A_{xy}, has no meaning unless limits are placed on the form that the coil may take; apart from some geometrical convention, it would be meaningless to say that the position of a long helix relative to some system was the same as that of a flat coil.

Let us therefore place limits on the form of the search coil and adopt the convention that all are to be "flat" and rigid, though they may differ in area and in the number of turns, and are to have one "marked" face. Then the position of any search coil relative to any coordinate frame fixed in the magnet is perfectly determinate when the position of its centre and the direction of the normal to the marked face are given; and we can inquire whether, if some particular state of the magnet and positions of the search coil are always used to define the unit, the value of A_{xy} is independent of the search coil used in measuring it and characteristic of the states of the magnet and positions relative to it. We find that it is so characteristic so long as the area of each coil is small enough, and that the permissible upper limit depends upon the magnet (i.e. on the uniformity of its field, in ordinary terms); so we adopt the further convention that, in measurements on any particular magnet, the area of the search coil must not exceed this limit. We thus arrive at a magnitude (in spite of the added conventions, it will still be denoted by A_{xy}), measurable independently of the measurement of any other magnitude, characteristic (for any given magnet) of pairs of positions around it, each position being defined by the situation of a point and the direction of a line drawn from that point.

The form of the law (2.1) on which the measurement of A_{xy} depends shows that, given any distribution of A_{xy}, it must be possible to find a set of magnitudes X_x, X_y each characteristic of a single position (not, like A_{xy}, of a pair of positions) such that

$$A_{xy} = k(X_x - X_y). \qquad \ldots\ldots(3.1)$$

But, unless something is added, the X's, unlike normal magnitudes, would involve an arbitrary additive constant, as well as the arbitrary scale factor k. This

difference would vanish if we could find facts or laws that distinguish one choice of the additive constant from all others, and thus make it no longer arbitrary, and especially if we could find a reason for attributing the value 0 to X_0, characteristic of some position or set of positions denoted by suffix 0.

Such a reason can be found. Suppose that the flat search coil is symmetrical about an axis lying in its own plane, so that on rotation through 180° about the axis the winding of the coil occupies the same space as before, but the normal to the unmarked face replaces that to the marked face; such a rotation will be called "reversal". Then experiment shows that, in general, reversal produces a response of the galvanometer, as does any other motion of the coil; but that for each point near the magnet there is a plane such that, if the marked normal originally lies in that plane, reversal produces no response; when this condition is fulfilled, the coil will be said to be in a "zero" position characterized by X_0. The plane and the zero position are, in general, different for different points, but if the coil is suddenly transferred from one zero position to another, no response occurs, and none occurs if it is suddenly transferred from one of these zero positions near the magnet to a point very distant from it, where any magnitude determined by the magnet would be expected to be zero.* All these facts support the idea that the value 0 should be assigned to every X_0, so that X_x characteristic of any non-zero position x will be A_{x0}/k, where A_{x0} is the reading on the calibrated scale when the search coil is suddenly transferred from x to a zero position.

The reader will no doubt have realized already that X_x, apart from a scale factor, is the familiar quantity that might be written $(B_n)_x$, i.e. the component of the flux-density normal to the small flat search coil when its centre is located at the point and its marked normal is turned in the direction characteristic of the position denoted by x; when B_n has been measured for all positions x, the fact that it is the normal component of a vector **B** will appear from a study of the measurements, and the complete distribution of **B** will be determined. Accordingly the final result of this discussion is to show that **B**, the flux-density (or magnetic induction), can be measured by methods that do not involve any measurement of any other magnitude (and, in particular, of any other magnetic magnitude), methods that involve only laws of equality and of addition together with conventions (namely the limitation to small flat coils) that are based upon real and definite experiments.

§4. FLUX-LINKAGE

The distribution of **B** round magnets of various kinds can therefore be determined by direct measurement, and it can be established that **B**, wherever it can be measured, is solenoidal, i.e. that the surface integral of its normal component over any closed surface is zero. It cannot be measured at all inside solid bodies, for small flat coils cannot be introduced into, or rotated within, solid bodies. It is tempting to assume that **B** is solenoidal, even where it cannot be directly measured, and if that assumption is made, **B** can be determined everywhere; for the distribution, within a closed surface, of a vector known to be everywhere solenoidal can be determined by calculation from values of the vector measured at appropriate points outside the surface. However, in Part II, §16, we had an example of a vector that is solenoidal in some regions but not in others; the general assumption must therefore not be made without adequate reason. Good reason for making the assumption so far as non-magnetic bodies are concerned

* The neglect of the earth's field here and elsewhere (e.g. §6) is justifiable because the experiments described could really be conducted in a space where the earth's field is neutralized.

(bodies that are air-equivalent in the sense of Part I, § 15) is immediately found; for direct experiment shows that if we take any system in air, for which **B** has been shown to be solenoidal, the mere insertion of non-magnetic bodies into any region of the system makes no difference to any response of the fluxmeter; in other words, bodies that are air-equivalent with respect to compass needles are also air-equivalent with respect to fluxmeters. Thus **B** is established as solenoidal and measurable throughout any system which is composed of non-magnetic materials only. In systems which include magnetic material, it is measurable and solenoidal in the air spaces, but we have as yet no evidence concerning points inside magnetic solids.

The further consideration of this matter is facilitated by the removal of the limitation to small flat search coils that was imposed in order to establish **B** as a measurable property. We therefore examine search coils of various shapes and sizes, and seek a law connecting the response of the fluxmeter with the magnitude **B** and the shape and size of the search coil. Experiment shows that a simple law can be found provided we limit it to search coils that satisfy the following conditions: (*a*) the wire must be so thin and the terminals so close together that the geometrical properties of the coil are completely represented by a single closed curve; (*b*) the resistance of the whole fluxmeter circuit shall remain unaltered when any change of coil is made. It is scarcely necessary to add that the coil must be constructed entirely of non-magnetic material, for this condition has been assumed throughout, any magnetic material included in the system always being regarded as part of the magnet. (This condition is of course always satisfied in practice.) We have already seen that the responses of a fluxmeter which includes such a search coil serve to determine a magnitude X characteristic of the state x of the system under examination. We can now establish a relation between X, the field of **B**, and the geometrical properties of the search coil. In practice, systems which are found to possess a uniform field of **B** throughout some particular region are of outstanding importance. It is found that the value of X for a search coil that lies wholly within such a region is determined only by the magnitude of **B** and the total projected area A of the search coil on a plane perpendicular to **B** (i.e., A is the area enclosed by the curve traced out on the specified plane by the projection of a point P on the coil as this point travels once completely round the winding from one terminal to the other). The law may be written

$$X = kBA, \qquad \ldots\ldots(4.1)$$

where the proportionality factor k is independent of the size, shape and orientation of the coil and of the field of **B** so long as the stipulated conditions are satisfied. This simple relation suggests the more general law, which is implied by calling **B** the flux-density at a specified point and X the flux-linkage of the search coil for the particular state of the system, that X is proportional to the surface integral Φ of the normal component of **B** over any continuous surface bounded by the closed curve along which the winding of the search coil lies. It must be noted that this surface integral only has a unique value for the closed curve if the distribution of **B** is solenoidal throughout the whole field. The application of the law to systems containing magnetic material therefore involves the assumption that **B** is solenoidal within magnetic materials. Now X can certainly be measured for many systems that include magnetic material, and the values are always uniquely associated with particular distributions of such values of **B** as can be measured, and they are, moreover, consistent in every way with a solenoidal distribution of

B throughout the system. The conception of **B** as a magnitude that is solenoidal throughout all magnetic systems whatever their composition is, therefore, fully justified by experiment, and since values of **B** inside a magnetic solid can, with this conception, be determined from measured values of X, we may legitimately regard **B** as measurable everywhere. The general law may be written

$$X = \Phi = \int B_n dS, \qquad \ldots\ldots (4.2)$$

the scale factor being omitted since the units of **B** and X are always chosen so as to make it unity. We shall therefore henceforward regard X and Φ as the same magnitude and use the same symbol Φ for both.

We may note here that Φ can be measured for search coils of any size and shape, but that for the measurement of **B** the coil must be small enough to lie wholly within a region throughout which **B** can be shown to be sensibly uniform; it must also possess a definite axis rigidly fixed with respect to the winding, and a determinate „effective area" A, which is its projected area on a plane perpendicular to this axis. Measurements of **B** can then be made in accordance with the law

$$\Phi = B_a A, \qquad \ldots\ldots (4.3)$$

where B_a denotes the component of **B** in the direction of the axis of the search coil.

§ 5. INDUCED E.M.F.: FARADAY'S LAW

At this stage it becomes practicable to establish Faraday's law of induction in the familiar form

$$e = k\, d\Phi/dt, \qquad \ldots\ldots (5.1)$$

i.e. the instantaneous E.M.F. generated in any search coil by a change of state of the system is proportional to the rate of change of flux-linkage of the coil. Instantaneous E.M.F. is of course a generalization of the magnitude E established in Part I, consistent with the instantaneous voltage and current of Part II. Thus e is defined as instantaneous open-circuit voltage and (5.1) can be considered as an experimental law that can be established by means of experiments with, say, a cathode-ray oscillograph calibrated as a voltmeter.

It is natural at this point to see whether e, like E, satisfies Kirchhoff's second law, and therefore accounts for the transient currents indicated by the galvanometer of the fluxmeter. However, it is sufficient to note here that Kirchhoff's law can only be applied to circuits of varying current if terms involving self-inductance and capacitance are included in addition to the ΣIR of the D.C. circuit. The detailed consideration of these matters is more appropriate to the laws of alternating current circuits than to magnetism, and we shall therefore not pursue them here.

Sometimes (5.1) is quoted as a definition of Φ, and not a true experimental law: we would therefore emphasize that we have some knowledge of Φ independent of this relation. It must also be remembered that (5.1) is not a complete statement of the relation between e and Φ for any circuit. If the circuit is not wholly filamentary, but passes through an extended conductor which is in motion, as in the Faraday wheel and Lorentz apparatus, an E.M.F. can be measured even when $d\Phi/dt = 0$. The complete law must be written

$$e = -\left\{\frac{\partial \Phi}{\partial t} + \int_e (\mathbf{B} \times \mathbf{v})\, dl\right\}, \qquad \ldots\ldots (5.2)$$

where $\partial\Phi/\partial t$ represents the rate of change in the absence of motion, and $\mathbf{v}$ is the velocity of the element dl of the material in the circuit relative to the field $\mathbf{B}$: that is to say, the complete law must include *both* "change of linkage" and "flux-cutting". The Lorenz method for the absolute determination of the ohm constitutes an accurate verification of (5.2), which, therefore, we also regard as an established experimental law. In (5.2) the proportionality factor k of (5.1) has been made -1, which is of course the usual choice, and serves the very important practical purpose of defining the unit of E by reference to the units of Φ and $\mathbf{B}$. It would be tedious to trace in detail the reason for the negative sign, but it may be worth noting that it is determined solely by conventions laid down in connection with other laws, e.g. that fixing the sense in which circulations are linked positively, and that prescribing that in any circuit an E.M.F. and the current it drives shall have the same sign.

The next problem is to decide by what the field of $\mathbf{B}$ is determined. Here we meet the conception of "magnetic materials", and some difficulties rather different in kind from those we have discussed so far. These are dealt with in the following paper.

The Experimental Basis of Electromagnetism— Part IV: Magnetic Materials

By L. HARTSHORN
National Physical Laboratory, Teddington

MS. received 3rd March 1949

ABSTRACT. This paper concludes the inquiry which was undertaken by N. R. Campbell and the author with the object of elucidating the connection between the concepts and principles of electromagnetism and the experimental operations actually performed in the laboratory that constitute their factual basis. In Part III the vector $\mathbf{B}$ was established as measurable everywhere, even within solid bodies. The vector $\mathbf{H}$ and the scalar $\mu=\mathbf{B}/\mathbf{H}$ are now shown to be measurable in special circumstances by means of the magnetometer and permeameter, but in general their values depend on a hypothesis, which is stated. The significant facts concerning the magnetic properties of real materials are briefly reviewed, and the two-fold aspect of the science is emphasized: the self-consistent mathematical theories based on postulates, on the one hand, and the complex of experimental laws on the other. It is important that the relation between the two shall be clearly established, and not merely assumed as self-evident.

§6. NON-MAGNETIC MEDIA*

In Part III of this inquiry we reached the stage at which $\mathbf{B}$ was established as a vector magnitude measurable independently of any other magnitude and characteristic of the states of certain systems, which we called magnets, and of position in and around them. We now proceed to consider what determines the distribution of $\mathbf{B}$, and for simplicity we shall restrict ourselves in the first instance to systems in which all the materials are non-magnetic. Since $\mathbf{B}$ is everywhere solenoidal, it can be determined experimentally at every point of the system. We can also readily show that $\mathbf{B}_0$ at any point (we shall use the suffix 0

* Section headings continue in sequence from Part III.

to indicate the limitation to non-magnetic media) is a linear function of the currents in the circuits of the system, and falls to zero when they all become zero. More generally, we observe that there is a very close connection between $\mathbf{B}_0$ and the magnitude $\mathbf{H}_0$, which was defined in Part I by the equation

$$\mathbf{H}_0 = S.I.\oint \frac{\mathbf{dl}\times\mathbf{r}_1}{r^2} = S.\mathbf{G}.I, \qquad \ldots\ldots(6.1)$$

and which therefore satisfies the equation

$$\oint \mathbf{H}_0\, dl = 4\pi SnI. \qquad \ldots\ldots(6.2)$$

Separate measurements of $\mathbf{B}_0$ and $\mathbf{H}_0$ enable us to establish with high accuracy the experimental law

$$\mathbf{B}_0 = \mu_0\mathbf{H}_0. \qquad \ldots\ldots(6.3)$$

In (6.3) μ_0 is a scale-factor without associated derived magnitude, since it has the same value for all non-magnetic materials. It plays the same part in (6.3) as does S in (6.1) and (6.2) and k in (5.1). By assigning convenient arbitrary values to each of these scale-factors, three units are defined in terms of other units. For example, in the M.K.S. system we assign to S the value $1/4\pi$, thereby defining the "ampere-turn per metre" as the unit of $\mathbf{H}_0$; we then assign to μ_0 the value $4\pi\times10^{-7}$, thus defining the unit of B by reference to the ampere-turn and metre, and then give k the value -1, thereby defining the volt by reference to the ampere-turn, metre, and second. The ohm is of course defined by reference to the volt and ampere by making the scale-factor in Ohm's law unity. A different choice of scale factors gives a different system of units, but all are on the same footing.

This use of the experimental law (6.3) to obtain a unit of $\mathbf{B}$ is clearly of the greatest practical importance, for apart from some such law, the independent method of measuring $\mathbf{B}$ would demand frequent reference to one or more fixed positions near some standard magnet in order to re-calibrate fluxmeters every time a change of search coil became necessary. In virtue of this law, every "air-cored" circuit that is accurately measurable in its linear dimensions and current becomes a standard magnet, i.e. a standard field of $\mathbf{B}$.

There is some evidence that a law of the form (6.3) remains true, but with some other constant replacing μ_0, if the medium surrounding the coils and filling the whole space in which $\mathbf{B}$ is distributed is uniform but not air-equivalent. Experiments of this kind are, however, only practicable in fluids at ordinary temperatures, and these are so similar magnetically to air that the differences in the measured quantities for different media are not usually much greater than the experimental error. The question of the existence of a derived magnitude characteristic of feebly magnetic materials is therefore best considered in relation to experiments of a different kind, which will be discussed later.

§7. MAGNETIC MATERIALS: PERMEABILITY

We pass now to a consideration of the systems for which (6.3) is not even approximately true, i.e. systems which include materials that are markedly not equivalent to air in their effect on fluxmeters and compass needles, the strongly magnetic solids. The evidence which showed $\mathbf{H}_0$ as defined by (6.1) to be a significant property of non-magnetic systems now no longer applies, but it is

convenient to denote by $\mathbf{H}_I$ the value of $S.\mathbf{G}.I$ of (6.1) for such a system. Very simple experiments with a fluxmeter show that **B**, far from being completely determined by $\mathbf{H}_I$ in accordance with (6.3), is frequently large when $\mathbf{H}_I$ is zero. For a given system it is, however, associated with $\mathbf{H}_I$ in the sense that they invariably change together, though $\Delta B/\Delta H_I$ is usually much greater than μ_0, and not obviously characteristic of any part of the system. Useful results have however been obtained by adopting the hypothesis that the vector **B** is always associated with a vector **H**, which in the special case of a non-magnetic medium reduces to $\mathbf{H}_0$, and which is such that the ratio $\mathbf{B}/\mathbf{H}=\mu$ is a scalar magnitude characteristic of the material at the point to which **B** and **H** refer. The fact that values of μ characteristic of various materials have been obtained provides some justification for the hypothesis. We must now examine the operation by which these values of μ and **H** are obtained, for according to our principles it is to these experiments that we must look for the meaning of these quantities.

Examination of the methods actually used for measuring μ shows that the one to which all others are referred consists in the use of the familiar uniformly wound long solenoid (or an equivalent toroid) and fluxmeter—the permeameter, for short. For simplicity we shall consider only the ideal form, a circuit in the form of an infinitely long solenoid, uniformly wound with N turns per unit length, and enclosing a search coil of effective area A_s, which forms part of a fluxmeter. The material to be measured takes the form of an infinitely long cylindrical core of cross-sectional area A_m; it is placed in the solenoid so that it is embraced by the search coil and so that its axis is parallel to that of the solenoid. Measurements are made by changing the steady current through the solenoid from a value I to a value $I+\Delta I$ and measuring the corresponding change of flux linkage of the search coil $\Delta\phi$ by means of the fluxmeter. The ideal is of course never completely attained, but since permeameters are only recognized as satisfactory when the inevitable departure from the ideal is concealed by the experimental error, it is unnecessary to consider such departures here.

It follows from (6.1) that H_I is zero outside the solenoid for all values of I, and inside it is everywhere $4\pi SNI$ and parallel to the axis; the solenoid is essentially a device for producing a uniform field of H_I. For simplicity we will adopt M.K.S. units so that this field is given by NI. Experiment shows that so long as the whole coil system is free from magnetic material, and the core is absent,

$$\Delta\phi=\mu_0 A_s N\Delta I. \qquad \ldots\ldots(7.1)$$

Indeed, it was mainly on evidence of this kind that (6.3) was based. When the magnetic core is introduced and the measurement repeated, $\Delta\phi$ is often greatly increased. Observations usually suggest a law of the form

$$\Delta\phi=\{\mu A_m+\mu_0(A_s-A_m)\}N\Delta I, \qquad \ldots\ldots(7.2)$$

where μ is much greater than μ_0, and depends on the nature of the core. For a class of material which is severely limited, but which includes some of technical importance ("constant-permeability alloys"), μ is found to be characteristic of the material and independent of A_m, NI and ΔI over a useful range of values. The law (7.2) shows that in a permeameter such materials have an effect which is exactly equivalent to an increase in **B**, throughout the space which they occupy, from the original value $\mu_0 H_I$ to μH_I. This μ is the magnitude which is called the permeability of the material, and by analogy μ_0 is often called the permeability

of free space. (It is convenient in practice to record the relative permeability $\mu/\mu_0=\mu_r$ since this ratio has the same value in all the ordinary systems of units.) We conclude that the general vector $\mathbf{H}$, whatever else it may be, is identical with H_I at all points in an ideal permeameter.

§8. THE MAGNETIC CIRCUIT

We must now consider how H is affected when there is a departure from the conditions of the permeameter, and for simplicity we shall, in the first instance, restrict ourselves to materials of constant μ. Let the material take the form of a solid ring which completely fills both the uniform toroidal winding and search coil: μ can be measured as B/H_I. Let now a narrow gap be cut in the material. Its effect is well known: the ratio $\Delta\phi/\Delta H_I$ is greatly reduced, but so long as the length of the gap l_0 is very small compared with the total length of the toroid l (both measured circumferentially) it remains independent of the position of the search coil, and we therefore conclude that $\mathbf{B}$ has the same value in the gap where the permeability is μ_0 and in the material where it is μ. If this value is B_2, then $\mathbf{H}$ must have the value B_2/μ in the material and B_2/μ_0 in the gap, and neither of these values is H_I. Thus $\mathbf{H}$ no longer satisfies (6.1): it is natural to see if it still satisfies (6.2). For this simple system (6.2) becomes

$$\frac{B_2}{\mu}(l-l_0)+\frac{B_2}{\mu_0}l_0=lNI. \qquad \ldots\ldots(8.1)$$

This law for the toroid with a small gap has been established experimentally, but it must be admitted that the experimental error is usually rather large.

Slightly more general formulae of this kind find useful application in electrical practice, and may therefore be considered as experimentally established. They are, however, limited to systems that can be described as magnetic circuits, i.e. systems in which the field of B is confined to a closed path of measurable length and cross section, the flux-linkage being constant for all cross sections, but $\mathbf{B}$ varying with change of cross section along the path. The circuit may be built up of various materials so that μ may change discontinuously from point to point along it, but μ must be uniform over any section that is everywhere perpendicular to $\mathbf{B}$. In the simplest case, the cross section of the circuit is everywhere small enough to justify the neglect of the variation of $\mathbf{B}$ over it; then at any point where the cross-sectional area is A, B is given by ϕ/A and H by $\phi/\mu A$, and both are directed along the circuit. If the circuit can be divided into portions of length l_1, l_2, $l_3 \ldots l_p$, each of uniform permeability throughout, the values being $\mu_1, \mu_2 \ldots \mu_p$, and the cross sections of the several portions $A_1, A_2 \ldots A_p$, then application of (6.2) yields the formula

$$\phi\{\Sigma_p l_p/(A_p\mu_p)\}=\Sigma_r n_r I_r, \qquad \ldots\ldots(8.2)$$

where I_r denotes the current in the rth current circuit linked with the magnetic circuit and n_r is the "number of turns" in this linkage. By analogy with Kirchhoff's second law, $\Sigma_r n_r I_r$ is called the magnetomotive force of the system, and the quantity in brackets the reluctance of the magnetic circuit, which is given as the sum of the reluctances of the several portions which are in series-connection in the circuit. Systems of large cross section can often be dealt with by applying (8.2) to elementary tubes of flux of small cross section into which the circuit can be divided. The details need not concern us; $\mathbf{H}$ is seen as a useful conception in making calculations of this kind, and they are certainly

important in practice; but it will be noted that **H** is only used as an auxiliary variable which does not appear in the result: we must therefore look further for evidence of its significance in terms of experimental operations.

§9. THE *B–H* HYPOTHESIS

The existence of two vectors **B** and **H**, each having a determinate value for points inside solid bodies, cannot be considered as completely established by experiment. Examination of the methods usually employed for determining **B** and **H** suggest that they depend on a hypothesis that we shall call the *B–H* hypothesis, and shall state in a general form as follows:

Any point in a system of current circuits and material bodies is characterized by the following magnitudes:

(*a*) The vector **B** determined by measurements with a fluxmeter and the equation

$$\operatorname{div} \mathbf{B} = 0. \qquad \ldots\ldots(9.1)$$

(*b*) A scalar μ and a vector **H** which are uniquely determined by the equations

$$\mathbf{B} = \mu \mathbf{H} \qquad \ldots\ldots(9.2)$$

and

$$\oint \mathbf{H}\, dl = \Sigma_r n_r I_r, \qquad \ldots\ldots(9.3)$$

where I_r is the steady current circulating in the rth circuit, and n_r is the number of times which the path around which the integral is taken is linked in the positive sense with the rth circuit.

It is to be noted that the experimental laws that are well established, viz. those for non-magnetic media, for the permeameter and for the toroid with a narrow gap are merely the results obtained when this hypothesis is applied to specially simple cases. This hypothesis therefore constitutes the definition of the general vector **H**.

The question what limitations are necessary and sufficient to ensure that the above three equations determine a unique distribution of the three magnitudes **B**, μ, **H** is of purely mathematical interest and therefore outside the scope of this paper.

§10. THE MEASUREMENT OF H

We have seen that **B** is (in principle) measurable everywhere. Can the same be said of **H**? In the special cases of (*a*) the system that contains no magnetic material and (*b*) the permeameter, **H** becomes equal to $\mathbf{H}_I$ and is therefore measurable in terms of current. In the more general case **H**, unlike $\mathbf{H}_I$, is not solenoidal and therefore cannot be obtained from the values of current. If the permeability is known **H** can of course be calculated as $\mathbf{B}/\mu$, but unless this ratio has some other significance nothing is gained by giving it a special name: indeed, **H** becomes no more than an auxiliary mathematical variable.

A possible method of measuring **H** directly is suggested by the experiments which originally led to the definition of $\mathbf{H}_0$ by (6.1), viz. experiments concerning the torque T on a small compass needle in air. Within the experimental error it is given by

$$T = SI\mathbf{G} \times m = \mathbf{H}_0 \times m, \qquad \ldots\ldots(10.1)$$

where m (the moment) is a derived magnitude characteristic of the needle. The suggestion is that we can measure $\mathbf{H}$ at any point by observing the torque on a compass needle of known moment at that point, in virtue of a law

$$T = \mathbf{m} \times \mathbf{H}. \qquad \ldots\ldots(10.2)$$

Measurements of this kind are certainly made in practice, but they are necessarily severely limited in scope, for compass needles cannot be inserted into solid bodies. In actual practice $\mathbf{H}$ can only be measured by this method at points in air, and for most magnets the range of $\mathbf{H}$ over which m in (10.2) proves to be a constant for the particular magnet is very small. Nevertheless the method can be used for the measurement of $\mathbf{H}$ over a very wide range if m in (10.2) is treated, not as a constant, but as a function of $\mathbf{H}$ characteristic of the particular magnet. Special magnets have been made for which this function is single-valued over a very great range of $\mathbf{H}$, so that the value of m in (10.2) corresponding to any observed value of T can be determined by an auxiliary measurement in a standard solenoid. In practice the instrument is calibrated in this way to indicate $\mathbf{H}$ directly.

Thus $\mathbf{H}$ can be determined by such operations at points in an air space, even one included in a system of strongly magnetic bodies, and provided the small suspended magnet is not allowed to approach too closely to the surface of a strongly magnetic body the values are always found to be equal to B/μ_0, and to be consistent with the B–H hypothesis.

It is interesting to note that these instruments for measuring $\mathbf{H}$ are usually called fluxmeters, a term normally associated with $\mathbf{B}$ rather than $\mathbf{H}$. This has arisen because they are always used in air-spaces where $B = \mu_0 H$, and are generally calibrated in the system of units for which $\mu_0 = 1$. The use of this system often leads to the notion that in any air-space B and H are identical. The facts are, that they are different in the sense that the operations by which they are measured are different, but they are "the same magnitude" in the sense in which this term was used in Part I.

The well-known methods of measuring $\mathbf{H}$ at points near the surface of solid bodies by means of very narrow search coils closely fitting the surface, or by means of the magnetic potentiometer, are equivalent to measurements of B at points in air near the surface by means of a fluxmeter, and therefore call for no special comment.

Our general conclusion is that $\mathbf{H}$ is directly measurable in air-spaces, but since it is not in general solenoidal such measurements alone are not sufficient to determine values for points inside magnetic materials. Such values depend on the B–H hypothesis.

§ 11. MAGNETIZATION CURVES: HYSTERESIS

We have so far assumed that the materials under discussion all have a definite permeability μ, which is independent of $\mathbf{H}$ or $\mathbf{B}$. It is, however, well known that most strongly magnetic materials are so complicated in their behaviour that no single value of μ will give any adequate account of it. The permeameter is still the most generally satisfactory instrument for dealing with such materials, the law (7.2) being applied in the form

$$\Delta\phi = A_m \Delta B + \mu_0 (A_s - A_m) \Delta H, \qquad \ldots\ldots(11.1)$$

and values of ΔB corresponding to the values ΔH being deduced from the observations of A, ϕ and ΔI. Summations of the values of these increments (i.e. $\Sigma\Delta B$ and $\Sigma\Delta H$) in a manner too familiar to be detailed here enable us to assign a value

of **B** to each value of **H**, provided one such pair of values is known. A conventional procedure is usually followed in deriving these values, e.g. there is a preliminary "demagnetizing" treatment which general experience suggests will justify the assumption $\mathbf{B}=0$ when $\mathbf{H}=0$, and then the values of **H** follow a regular sequence between certain limits. It is an experimental fact that when such a procedure is followed, the relation between B and H can often be represented by a definite "magnetization curve" or a "hysteresis loop" that is characteristic of the material in the permeameter, that is to say, independent of the size and shape of the sample within the limits imposed by the permeameter, and dependent only on the composition and physical condition of the material. Thus the properties of strongly magnetic materials are represented, not by a constant μ, but by a characteristic function.

The details of the procedure need not concern us, but we must note that no law that purports to represent the magnetic behaviour of a material by a definite permeability μ is generally applicable to real magnetic materials. Such simple laws are applicable only to the relatively few "constant-permeability" materials. Nevertheless engineers often find it convenient to apply the simple formulae to their materials when they are used within a narrow range of magnetic conditions, and in such cases they adopt the simple expedient of interpreting μ as $\Delta B/\Delta H$ for changes of B and H which have been found empirically to represent the working conditions. Thus we meet the terms incremental permeability, initial permeability, reversible permeability, differential permeability, representing $\Delta B/\Delta H$ in accordance with various conventions. Such quantities cannot however be expected to have any wider significance.

It now becomes obvious that the determination of the distribution of **B**, **H** and μ by the application of the B–H hypothesis to a real system including strongly magnetic materials, is necessarily a very complicated matter. Instead of the constant μ first considered, we have now a function represented by a curve or a table of values, and not even a single-valued function of H in most cases. In such cases the application must be made by numerical computation, and μ must be interpreted as the value of the permeability ($=B/H$) given by the characteristic curve for the material occupying the point in question, for the particular value of **B** which satisfies equations (9.1), (9.2), (9.3). When the characteristic curve includes an appreciable hysteresis loop it gives more than one value of μ for each value of B, except at saturation, and computation is then only possible if the previous magnetic history of the system is known sufficiently well to indicate clearly which of the values is appropriate. A preliminary demagnetization (or magnetization to saturation) will often provide the necessary information, but the general problem is one of great complexity and a detailed solution for many actual systems is impracticable, although relaxation methods (Southwell 1946) would probably enable a wider range of conditions to be investigated than has so far been done. The direct evidence for the B–H hypothesis is obviously meagre, being limited to the simple cases already mentioned. It does however provide satisfactory coordination for a great amount of experimental work, and this constitutes its chief justification.

§ 12. SATURATION: INTENSITY OF MAGNETIZATION

There remains however an important experimental law that gives **H** a significance that is more than mathematical; it is the one suggested by the term saturation, mentioned in the last section. If in the permeameter the current

is steadily increased, then for the large class of strongly magnetic materials of § 11, provided the value of **H** exceeds some particular value which is different for different materials and can only be found by experiment, the relation between ΔB and ΔH_I satisfies the law (7.1), which can be written $\Delta B = \mu_0 \Delta H$; in other words, in this region the increments of ΔB and ΔH obey the same law as if the material were absent. Thus, beyond the particular value of **H**, the value of $B - \mu_0 H$ remains constant however much **H** is increased, and within this range of values **H** has the same significance within the magnetic material as it does within a non-magnetic material or air. Moreover, for many materials the stationary value of $B - \mu_0 H$ is found to be more accurately characteristic of the material than μ.

The most obvious interpretation of this law is that the material is an open structure of some kind in space, and that the total flux-density B when the material is present always includes a component $\mu_0 H$, which is the flux-density in that portion of space whether the material is present or not, so that $\mathbf{B} - \mu_0 \mathbf{H} = \mathbf{J}$, say, represents the contribution of the structure itself, and this contribution cannot exceed some limiting value J_s which is characteristic of the structure. The whole idea necessarily implies that B, H, μ and J only represent properties of the system on a scale that is macroscopic relative to the microscopic scale of the structure itself, but we have no reason for not accepting such a limitation to the significance of our measurements. J is of course the intensity of magnetization, and J_s the saturation magnetization. The general definition of J is the equation

$$\mathbf{B} - \mu_0 \mathbf{H} = S_J \mathbf{J}. \qquad \ldots\ldots (12.1)$$

The scale factor, S_J, is frequently chosen to be 4π instead of unity, but this is purely a matter of convention. The ratio $J/\mu_0 H$ is defined as the susceptibility, κ, of the material, and we have therefore

$$\mu_r - 1 = S_J \kappa. \qquad \ldots\ldots (12.2)$$

The susceptibility κ is therefore characteristic of the material to the same extent as μ_r, but J_s is often more accurately representative of the material than either. The fact that J has this significance in terms of experiment implies that the conception of **H** within a magnetic solid, on which it partly depends, is also not without physical significance.

§ 13. THE MEASUREMENT OF SMALL SUSCEPTIBILITY

The susceptibility of a non-magnetic material is zero by definition. It is well known that there is a very large class of materials that are nearly but not quite non-magnetic, and susceptibility provides a very convenient measure of the magnetic behaviour of these materials. In accordance with our principles we must examine the methods by which κ is determined for such materials in actual practice. The Gouy apparatus may be taken as typical. The material to be measured takes the form of a long straight rod of cross section A, permeability μ_r and susceptibility κ, suspended vertically from the beam of a balance in a medium of permeability μ_0. Its lower end lies in a strong uniform magnetic field H_1 (generally, but not necessarily horizontal); its upper end in a much weaker field H_0, which, if appreciable, must also be uniform. The field H_1 can be removed and established at will, and the force F on the specimen associated with the field H_1 is determined by observation of the increase of weight indicated by the balance

when the field is established. The law established for the method may be written,

$$F = A(\mu - \mu_0)(H_1^2 - H_u^2) \qquad \ldots\ldots(13.1)$$

or

$$F = S_f \kappa \mu_0 A(H_1^2 - H_u^2). \qquad \ldots\ldots(13.2)$$

Thus the measured force is proportional to κ, other things being equal, which is no doubt why the method is usually regarded as one for determining susceptibility rather than permeability. The materials for which the law has been accurately established fall into two classes: the paramagnetic materials for which κ is positive and the diamagnetic materials for which it is negative. For both classes it is usually much smaller than unity, and it is for this reason that μ_r $(=1+4\pi\kappa)$ is an inconvenient magnitude for discriminating between materials in these classes.

In writing (13.1) and (13.2) we have tacitly assumed that μ and H are the magnitudes that we have already defined in terms of the permeameter and the B–H hypothesis and that the scale factor in (13.1) is unity for the units already chosen. All the available evidence is consistent with this law, and it is fairly convincing, because a slight modification of the permeameter technique, described previously, enables us to measure $(\mu - \mu_0)$ with accuracy for specimens of the same form as are required for the Gouy method. A long solenoid and a search coil of many turns are employed; a large current giving an intense field in the solenoid is established; the fluxmeter circuit, previously open, is then closed, and the specimen suddenly withdrawn from the search coil. In these circumstances the change of flux-linkage ϕ measured is given by

$$\Delta\phi = A_s(\mu - \mu_0)H_I, \qquad \ldots\ldots(13.3)$$

and since both A_s and H_I are very large $(\mu - \mu_0)$ can be accurately determined although it is very small. This is indeed another standard method for the measurement of κ, and one that is of great importance in enabling us to establish that κ, as measured by the Gouy and Faraday methods and their variants, is "the same magnitude", in the sense in which we employ that term, as $\mu_r - 1$ measured by the permeameter or determined by the B–H hypothesis.

§14. ENERGY OF THE MAGNETIC FIELD

The law of the Gouy method calls for some consideration of the conception of the energy associated with the magnetic field. When the field is wholly due to currents in a non-magnetic medium, it follows from (4.1), (6.1) and (6.3) that the magnetic flux through the rth circuit due to the currents in the others is given by

$$\phi_r = \Sigma_s M_{rs} I_s, \qquad \ldots\ldots(14.1)$$

where

$$M_{rs} = (\mu_0/4\pi)N \qquad \ldots\ldots(14.2)$$

and N is Neumann's integral for the rth and sth circuits. Here and in what follows we insert the scale factor appropriate to M.K.S. units unless the contrary is stated.

It now follows from (5.1) that if e_r is the instantaneous E.M.F. induced in the rth circuit

$$e_r = \Sigma_s M_{rs}\, dI_s/dt \qquad \ldots\ldots(14.3)$$

and

$$\int -(\Sigma_r e_r I_r)\, dt = \tfrac{1}{2}\Sigma_r \Sigma_s M_{rs} I_r I_s = W, \qquad \ldots\ldots(14.4)$$

and if this E.M.F. has all the properties of direct E.M.F. the quantity W will be the energy that must be expended in order to start the currents, apart from that required to maintain them, and also the energy that will appear as heat or in some other form when the currents are stopped. There is strong experimental evidence for these laws taken together; M_{rs} proves to be accurately measurable in virtue of (14.3) and the values are consistent with (14.2) to a very high order of accuracy; also Ampère's law is obtained by taking the appropriate derivative of W, which may therefore be accepted as a "force function" for such systems.

If now the system includes magnetic material of constant permeability, and if M_{rs} now means the quantity defined by (14.3)—the mutual inductance, which is accurately measurable by, say, A.C. technique—then we find that (14.2) is no longer true. The experimental evidence suggests that for uniform media of constant permeability μ the law becomes

$$M_{rs}=(\mu/4\pi)N. \qquad \ldots\ldots(14.5)$$

It follows from the B–H hypothesis that for systems which include such materials we have

$$W=\tfrac{1}{2}\Sigma_r\Sigma_s M_{rs}I_rI_s=\tfrac{1}{2}\int\mu H^2\,d\tau, \qquad \ldots\ldots(14.6)$$

where $d\tau$ is an element of volume and the integration is taken throughout the whole region where the integrand is non-zero. All the experimental evidence supports the conclusion that W is a force function and that $F_q=\partial W_F/\partial q$ gives not only the forces tending to move and distort circuits, but also those tending to move magnetic material in their field. The Gouy method is one example. When we turn to the more complicated magnetic materials, we find hysteresis effects; the systems can no longer be considered as conservative and no force function can be regarded as established. A familiar argument shows that the energy that must be expended in order to change the magnetic induction from B_0 to B is given by

$$W=\int d\tau\int_{B_0}^{B}H\,dB, \qquad \ldots\ldots(14.7)$$

and this leads to the conclusion that during cyclic magnetization the energy lost per cycle per unit volume of material is determined by the area of the hysteresis loop. This conclusion is supported by the experimental evidence obtained by measuring the power loss by calorimeter and other methods, but the accuracy is not very high since power arising from other causes is nearly always a disturbing factor. The position is that the concept of a distribution of energy throughout materials finds little application in experiments on real magnetic material magnetic apart from those that have a constant permeability.

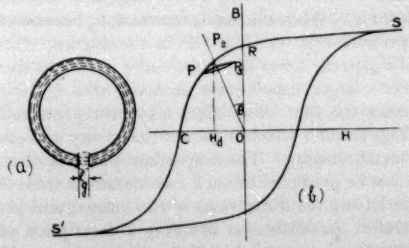
In order to complete our survey of the methods in general use for the measurement of magnetic properties, it will be necessary to consider the use of the magnetometer for this purpose. The term magnetometer is commonly applied to any instrument the use of which involves a measurement of the torque T exerted on a suitably suspended permanent magnet. We have already considered the use of such instruments for the measurement of H in air: the Schuster magnetometer was mentioned as an important instrument of high precision in Part I, and the "fluxmeters" mentioned in § 10 above can also be regarded as magnetometers. The historic Kew magnetometer and the magnetometers employed for measurements of μ or κ involve an additional law, that concerning the torque exerted

by one magnet on another, and it is this law that we must consider. But before doing so it will be well to consider the properties of "permanent magnets", using this term in the sense in which it is used in magnetometry.

§ 15. PERMANENT MAGNETS

The historical development of magnetism was based on the conception of the permanent magnet characterized by a definite axis and constant moment. We have employed the conception so far as to refer to compass needles, for which a derived vector magnitude **m** can be established in restricted conditions; indeed, "magnetometer needles" having this property are familiar enough to all physicists, but as we have already mentioned, the experimental evidence contradicts any idea that **m** can be regarded as constant for any given magnet; in particular, it must be expected to vary with **H** and μ in its immediate vicinity. It was no doubt for this reason that the magnetometer gave place to the fluxmeter as the standard instrument in this field of work. (It is interesting to note that even as late as 1902 the fluxmeter, although its principle had long been known, was treated in the *Handbuch der Physik* as entirely subsidiary to the magnetometer.) Instruments of the "moving magnet" type are however still of practical, as well as historical, importance, and the properties of the magnets actually employed must therefore be considered.

The most detailed information is that provided by the technicians who design and make such magnets, and we find that the results of their work, which naturally proceeds on empirical lines, can be summarized as follows. Permanent magnets of all forms, including the needle, are most conveniently regarded as magnetic circuits composed of two elements in series, one of a material specially chosen because its characteristic hysteresis loop is of large area and suitable shape, and the other an air path which may be of any form, from a narrow gap in a circular magnet to the air return path from one end of a needle to the other. The term magnet is commonly applied to the circuit-element of strongly marked hysteresis, but the air path is an essential feature. The properties of the magnet can best be understood by considering the procedure followed in making it, and for simplicity we will consider the case of a circular magnet of small and uniform cross section, with a narrow air-gap (see Figure). The gap is first completely filled



with material of very high permeability (soft iron), and the ring, having been provided with a suitable winding, is magnetized to saturation by passing a heavy current through the winding. If now the current is varied cyclically between this saturation value and an equal but oppositely directed one, the behaviour of the material can be represented by the hysteresis loop shown in the Figure. *B* and

H will not be quite uniform over any cross section of the magnet, but we may suppose them to be the values for the material within a central tube of flux of small cross section. The curve can be determined by the methods previously discussed, and we find that by first switching on the current corresponding to S and then reducing it to zero (switching off) we bring the material into the condition represented by R. If now we remove the soft iron from the gap we find that there is a reduction of flux corresponding to the attainment of a condition represented by P. The magnet is now complete: the winding can be removed, and experiment shows that the flux $\phi = BA$ of the magnet remains constant so long as the magnet is not disturbed. The value is, however, liable to change with change of temperature, mechanical shock, and especially with the application of any field of H or any change in the reluctance of the air gap of the magnet, e.g. the introduction of any material not air-equivalent. An applied negative H brings the material down the loop to P_2; a positive H takes it along a branch curve to P_3, while cyclic variations of H take it round a succession of subsidiary loops, each successive member being slightly lower than its predecessor, until a stable condition is reached. The final state is always represented by some point on or within such a subsidiary loop, and this state may be regarded as the working condition of a magnet in practice. For a good magnet the subsidiary loop is thin and only slightly tilted with respect to the H axis, so that ϕ, although not strictly constant, is, to the accuracy that is possible in much experimental work, a single-valued function of H.

The hysteresis loop is characteristic of the material from which the magnet is made, and is the same for magnets of all sizes and shapes, although in using it one must allow for any variation of B from point to point in magnets, which, unlike the simple example quoted, do not possess an approximately uniform distribution of B.

The position of the point P may be calculated as follows. Let l denote the length of the magnet along the central tube of flux and l_g that of the gap. When the magnetizing current is reduced to zero we have by the B–H hypothesis

$$Hl + Bl_g/\mu_g = 0; \qquad \ldots\ldots(15.1)$$

thus

$$H = -(l_g/l\mu_g)B. \qquad \ldots\ldots(15.2)$$

When the gap is filled with soft iron μ_g is very large and, therefore, $H = 0$, corresponding to the point R. When the iron is removed, μ_g becomes μ_0, and equation (15.2) can be represented by the line OP in the Figure, where $\tan\theta = l_g/l\mu_0$. Thus the wider the gap, the lower down the curve is P. As the gap widens the flux ϕ spreads over a larger area, i.e. the sectional area of the magnetic circuit increases as we enter the gap. The effect may be represented by dividing B in (15.2) by a leakage factor α which is greater than unity and can be determined from fluxmeter measurements. The important point is that the properties of actual magnets can be predicted by such considerations from the characteristic curves of the material and the dimensions of the magnet and its air path. The principles are therefore established as affording a description of the properties of real magnets that is consistent with all the known facts. High accuracy is impossible except in very limited conditions.

§16. THE MAGNETOMETER: MAGNETIC DIPOLES

A magnetometer is essentially a permanent magnet supported so as to be capable of rotation about an axis of symmetry that is perpendicular to the axis of its air path. Such magnets have already been taken for granted as familiar

objects adequately described by the term "compass needle", and we have shown that they can be used to measure H in air spaces in virtue of an experimental law,

$$T = \mathbf{m} \times \mathbf{H}, \qquad \ldots\ldots(16.1)$$

valid over a range of $\mathbf{H}$ that must be found by experiment for the particular magnet used. It can now be added that the deviations from the law that are observed in conditions that are beyond the range established for the instrument are consistent with the laws of permanent magnets described in the previous section.

The magnetometer "needle" may take the form of the ring with a narrow air gap there discussed: it is only necessary that the axis of suspension shall pass symmetrically between the walls of the gap. It is then found that the moment of the magnet $\mathbf{m}$ is given by

$$\mathbf{m} = \mathbf{B}Al_0, \qquad \ldots\ldots(16.2)$$

and that the conditions under which $\mathbf{m}$ can be treated as constant can therefore be obtained from the B–H curve for the magnet.

Alternatively, the magnet may be literally of needle form, or rather a straight bar of uniform cross section A and of length l, which is large compared with the dimensions of the cross section. Such magnets are prepared by a process analogous to that described for the circular magnet; the magnetizing winding takes the form of a long solenoid instead of a toroid and the closed magnetic circuit may consist of two such bars, each with its own solenoid, and with their ends linked by pieces of soft iron. Again we magnetize the circuit to saturation, switch off the current, and remove the soft iron links; the changes in the value of B are exactly similar to those for the ring, and can be represented in the same way by the portion RPC of the hysteresis loop, though in this case the calculation of the point P, which represents the working condition of the magnet, is not so simple. It is found, however, that magnets made from a given material can be usefully represented by a single curve RPC, and values of $\tan\theta$ characteristic of the shape of the magnet, increasing, for example, consistently as the magnet becomes shorter, other factors remaining constant. Similarly magnets of a given shape but different materials have properties which are consistent with a constant value of $\tan\theta$ applied to the "demagnetization curves" characteristic of the several materials. A magnet in its working condition is therefore regarded as characterized by the demagnetization curve for the material; and a demagnetizing factor $D = \tan\theta$, dependent on the shape of the magnet, and determining a demagnetizing field $H_d = -DB$, which is identified with H defined by the B–H hypothesis. The long thin needle and the ring with the narrow gap are the two forms for which D is small and B nearly uniform throughout the material. D increases as the needle becomes shorter and as the gap in the ring becomes wider; and in both cases the distribution of B at the same time departs from uniformity, the lines of flux opening out, with a consequent diminution of B, as they pass from the material into the air path. Thus in any permanent magnet made according to the standard procedure B increases as we pass along the magnet from the air path and reaches a maximum value in a central region, which is larger the longer the magnet or the narrower the air gap. The values of B and of $\phi = BA$ for this central region can be measured accurately by slipping the search coil of a fluxmeter off the magnet, and it can be shown by experiment that long needle magnets conform to the law

$$\mathbf{m} = BAl. \qquad \ldots\ldots(16.3)$$

For these magnets, $D=0$ and $H_a=0$, so that in the working condition $B=J$, and we may also write $\mathbf{m}=\mathbf{J}Al$. The same argument applied to the ring magnet with a narrow gap leads to $\mathbf{m}=\mathbf{J}Al_0$. These two equations show clearly that we must not define J as "magnetic moment per unit volume" if we are thinking of quantities that are actually measurable, for the relevant volume in the latter case is that of the air gap and in the former that of the magnet.

Another law established by means of the magnetometer is that concerning the torque exerted by one magnet on another. It is most conveniently expressed by the following experimental law for magnets of needle form: A permanent magnet of moment $\mathbf{m}$ is associated with a field of $\mathbf{H}$ in the space surrounding it, the value at any point P being given by

$$\mathbf{H}=S\,\mathrm{grad}\,\{(\mathbf{m}.\mathbf{r}/r^3)f(l,r)\}, \qquad \ldots\ldots(16.4)$$

where $\mathbf{r}$ is the radius vector OP, O being the centre of the axis $\mathbf{l}$ of the magnet, and f a function that is known, but need not be considered beyond saying that it tends to 1 as $l/r\to 0$. This field is superposed on any field that may exist at P in the absence of the magnet. (It would be well to note at this point that $\mathbf{H}$ in (16.1) is the value at the point in question in the absence of the magnet.)

It is scarcely necessary to trace in detail the experiments required to justify this law. Every physicist will recognize that the standard procedure associated with the Kew magnetometer will provide much of the evidence required. The well-known use of the magnetometer method for determining magnetization curves and hysteresis loops is also to the point. We must note that the law holds good for long solenoids, either with or without cores of magnetic material, as well as for permanent magnets, if we apply (16.3) to such solenoids. Results obtained in this way are consistent with those obtained with the permeameter, and this agreement also provides some support for the conception of magnetic moment as an important quantity. The theoretical conception of the magnetic dipole is derived directly from this conception and (16.4) in the limiting case when $f(l,r)=1$. The dipole is indeed defined as an entity of very small dimensions which obeys the equation

$$\mathbf{H}=S\,\mathrm{grad}\,\{(\mathbf{m}.\mathbf{r}/r^3)\}, \qquad \ldots\ldots(16.5)$$

where $\mathbf{m}$ is constant. This is exactly the same equation as was obtained for a current I circulating in a small circuit of area A surrounding the point O in a vacuous medium if $\mathbf{m}=IA$, and has the direction of the normal to the surface A (Part I, §15). It follows that the magnetic dipole can be conceived as either a minute current whirl or a minute permanent magnet in a vacuous medium. In either case we must assume that the dipole differs from the corresponding real object not only in the smallness of its dimensions, but also in freedom from resistance in the case of the current whirl, and freedom from all changes of moment in the other case. The magnetic field of a real circuit can be shown to be the same as that of a surface distribution of such dipoles, which is the "magnetic shell" of the old treatises. It is scarcely necessary to point out that the shell has by definition properties entirely different from those of real permanent magnets.

It is well known that the law of the torque between dipoles is mathematically equivalent to a law for point poles of the same form as those for point masses and point electric charges, and this has led to the development of mathematical theories in which the point pole with this law of force is the basic postulate. Such theories are quite divorced from the experimental basis of the subject as

we understand it, but the law is so frequently quoted as the fundamental experimental law of magnetism that it is impossible to ignore it completely. The most curious thing about the law is that even today, after generations of experiment, there is no general agreement about its exact form. There are two schools of thought: one stating the law in the form

$$F = Sq_1q_2/d^2, \qquad \ldots\ldots(16.6)$$

where S is a mere scale-factor or universal constant, the same for all materials, and the other in the form

$$F = Sq_1q_2/\mu d^2, \qquad \ldots\ldots(16.7)$$

where μ, the permeability, varies from one medium to another. Self-consistent theories can be built up from either law by making the assumptions necessary to secure some sort of correspondence with the known experimental facts. One law requires the recognition of "induced charges" in the medium, also subject to the law, while the other does not. Livens (1947) has recently discussed the matter in detail and has decided in favour of (16.6) on the grounds of the simplicity, scope, and generality of the resulting theory, which is essentially the original theory of Poisson, Kelvin and Maxwell. It is no part of our purpose to question his decision; we would only point out that the other law has been so widely quoted as fundamental in recent years that one can only make sense of the situation by recognizing that these are not experimental laws at all.

§ 17. CONCLUSION

We have now completed our survey of the operations which are most widely employed in experimental investigations of magnetism, and which therefore give the basic concepts of the science their meaning. The further development of the subject depends largely on mathematical theory, the form of which is dictated by mathematical operations rather than experimental operations. The theory takes the form of a self-consistent body of mathematical doctrine which, proceeding from certain postulates, is found to contain relations of the same form as the experimental laws. The theory is therefore accepted as a working mathematical model of the world of the experimenter, certain of the mathematical concepts being identified with the corresponding physical concepts. It is not to be expected that the basic postulates of the theory will correspond with the experimenter's basic concepts, and we have shown that they do not; the magnetic dipole or the point pole which forms the starting point of many theories is remote from the experimental basis of the subject and, provided the fact is recognized, there can be no objection to the procedure. We should, however, not confuse the laws of force between poles or dipoles with experimental laws; neither should we assume that because certain parts of the theoretical model correspond with the real thing that all its parts necessarily have their counterparts in the real world. It is from this point of view that our work should be considered. We believe that the actual correspondence between the experimental laws and the theoretical concepts requires a much closer scrutiny than is usually given to it. The self-consistency of a theory, although of great importance, affords no evidence whatever of its relevance to experiment; that evidence must be sought independently by actual examination of experiments. Self-consistency of the theories has always been examined with great care: consistency among the experimental concepts and the actual correspondence between those of theory and experiment

are too frequently taken for granted. It is sometimes said that these things are known by "physical intuition", a quality that can be cultivated by practice but not described. To us it seems to be only a cloak for a certain mistiness of thought which is out of place in physics, and which it is our chief aim to dispel.

REFERENCES

CAMPBELL, N. R., and HARTSHORN, L., 1946, *Proc. Phys. Soc.*, **58**, 634 ; 1948, *Ibid.*, **60**, 27.
LIVENS, G. H., 1947, *Phil. Mag.*, Ser. 7, **38**, 453.
SOUTHWELL, R. V., 1946, *Relaxation Methods in Theoretical Physics* (Oxford : University Press), Sec. 85.

DISCUSSION

Dr. N. R. CAMPBELL. The fundamental difference between Dr. Hartshorn and myself which has prevented my sharing with him the authorship of his last paper (IV), as I have that of our earlier papers I, II, III, concerns the significance of his " general vector " **H** ; we are perfectly agreed concerning **B** and $\mathbf{H}_I$.

1. I do not think it desirable to denote by **H** the vector, measured by the torque on a compass needle, that is the subject of IV, § 10. When it is measured in an air space it is the same " magnitude " as **B** in the sense of I, § 10, this being the only sense in which that term seems to me useful. Theorists have discussed* elaborately what the vector would be if it could be measured in a space filled with appreciably magnetic matter, and have usually concluded that it would differ from **B** by a factor involving μ for that matter ; it has been suggested that its relation to **B** would differ according as the field was due to currents or to permanent magnets. None of these speculations have any experimental support ; it seems to me foolish to introduce a special symbol in order to express them. I should therefore denote the magnitudes of IV, § 10 (in suitable units), by **B** and call it flux density.

2. If this were done, **H** would always mean the auxiliary variable characteristic of the *B–H* hypothesis, which I should prefer to state thus :—It is possible to calculate the distribution of **B** about any collection of current circuits and magnetic bodies by assuming (*a*) that **B** is everywhere solenoidal, (*b*) that it is associated at each point with a vector **H**, of which it is true (*c*) that

$$\oint \mathbf{H}\, dl = \Sigma_r n_r I_r$$

and (*d*) that it is related to **B** at each point in the same way as $\mathbf{H}_I$ is related to **B** in a permeameter whose core consists of the material occupying that point.

3. The appearance of **H** in a proposition would then be an indication that the *B–H* hypothesis was involved in it. This would justify some unexpected appearances. Thus in IV, § 13, the field is usually measured by a fluxmeter (in the sense of III, § 2) ; it might seem therefore that **B** would be more appropriate than **H** in IV, (13.1). But the flux density is measured in the absence of the magnetic material. Now it is a consequence of the *B–H* hypothesis, not often stated explicitly, that, if a *small* quantity of magnetic material is introduced into an air-space in which **B** has been measured, then, though the introduction will in general change both **B** and **H** everywhere, in the neighbourhood of the material introduced, the change of **H** will be much less than the change of **B**. Accordingly, by expressing IV, (13.1) in terms of **H**, not **B**, we make sure that the unknown error, due to making no allowance for the effect of the material on the field, is as small as possible.

4. Research during the last generation, by revealing the existence of " domains ", has shown that no piece of ferromagnetic material as large as a permeameter core can be homogeneous ; it cannot be truly characterized by a single parameter or function ; the *B–H* hypothesis cannot really be true of it. Since **H** derives its significance from the *B–H* hypothesis, it cannot really be applicable to bulk material.

5. The best that can be said of the hypothesis and the magnitude dependent on it is that they are valid over the whole of some practically important range of experiment, so long as no methods of measurement are used more precise than those normally employed in such

* See e.g., H. Chipart, *C.R. Acad. Sci. Paris*, 1921, **172**, 589–591, 750–753; L. R. Wilberforce, *Proc. Phys. Soc.*, 1933, **44**, 82–86; L. Page, *Phys. Rev.*, 1933, **45**, 112–115.
These authors, though all professing to expound the same classical theory, differ notably in their conclusions.

experiment. But I submit that even this is not true. The B–H hypothesis is of no practical use unless some subsidiary simplifying hypothesis is made about the B–H relation. Thus the conception of a magnetic circuit, having reluctance and containing M.M.F., is valueless unless it is assumed that B/H is constant; that can almost always be shown to be false by the very experiments used to determine the constant value or by some slightly modified variant. Again, the assumption of constant μ, involved in attributing a definite inductance to a coil with a dust-core, is almost always accompanied by the contradictory assumption that the core material has "hysteresis loss". Again, in Evershed's theory of permanent magnets (which theorists conspire to neglect, although it is much more important practically than propositions to which they devote reams of paper, and at least equally nearly true), the B–H relation is identified with the demagnetizing branch of the hysteresis curve; this, of course, is true only for very small changes.

6. I admire the gallantry and ingenuity of Dr. Hartshorn's attempt to base the significance of **H** on constant-permeability alloys and the extension of the hysteresis curve beyond saturation. But he will hardly convince anyone who remembers that the facts on which his defence rests were unknown until his **H**, and the "classical theory" on which it rests, had been established for at least two generations, and even now are not usually recorded in text-books. The real position, I suggest, is that the theory has been taken seriously only because it was propounded before any of the important facts about ferromagnetism were known, and because, by the time that those facts were discovered, Maxwell's reputation was so firmly based on other work that anything he said had become (and has remained for most physicists) outside the range of dispassionate examination.

7. The analogy between magnetic materials and dielectrics, which was undoubtedly one of the foundation stones of the classical theory, is invalid in respect of the matters considered here. The concept of permittivity has survived the discovery that all dielectrics are imperfect, because their imperfection can be represented by the substitution of a complex for a real permittivity; there is no analogous way of representing the fact that B/H_I is not single-valued.

8. If, as I maintain, the sole use of **H** is to make statements about magnetic materials that are either definitely false or unsupported by any evidence, it is particularly out of place in a theory that explains away magnetic materials as the electron theory explains away dielectrics. The essence of the modern theory of magnetic materials is that certain atoms are dipoles of zero dimensions, having magnetic moments independent of the field in which they find themselves; their behaviour is governed by equations of the form of IV, (15.1), (15.4)—the latter expressed in quantum-theory terms—by which it is possible, in the Kew magnetometer, to measure both of the vectors **m**, **H** without measuring any other magnetic magnitude. **H** so measured turns out to be the same magnitude as **B**; for in the presence of magnetic materials the equations cease to be true and **H** to be measurable by this method. Since the theory which explains magnetic materials cannot suppose that there is magnetic material in the field of the dipoles representing magnetic material, the vector **H** concerned in it cannot fail to be the same as **B**; nowadays it is sheer perversity, based on the accidents of history, to represent it otherwise.

I do not say that all propositions about theoretical dipoles to be found in current literature remain true if **B** is substituted for the usual **H**. But if they do not, then there must be some error or ambiguity that requires the attention of experts.

Dr. L. HARTSHORN (in reply). In view of the lamentable death of Dr. Campbell before these notes have appeared in print I think it more appropriate to outline the circumstances in which they were written than to attempt to reply in detail. The two papers III and IV were originally drafted by me as a single paper based on earlier drafts prepared by Dr. Campbell and extensive discussions with him. My expectation was that the whole would be published as a joint paper after Dr. Campbell had made whatever amendments he found necessary. This was his own idea also at first, but after a careful study of the matter he came to the conclusion that although he had little objection to anything actually stated in the paper, it showed that our views were essentially divergent. He therefore abandoned the attempt to produce an amended version on which we could be unanimous, and suggested that the form in which the papers now appear should be adopted. The difficulties raised by Dr. Campbell seem to me either unimportant or adequately covered by Part IV, but I am glad that it has been possible to state them in his own words, so that points that I may have missed are faithfully recorded.

Temperature Variation of the Electrical Properties of Nickel Oxide

By R. W. WRIGHT and J. P. ANDREWS
Queen Mary College, London

MS. received 17*th January* 1949

ABSTRACT. An experimental method of preparing specimens of NiO in the form of coherent strips is described. Simultaneous measurements of electrical conductivity σ and Hall effect R are then made at various temperatures up to about 700° c. and the thermo-electric power dE/dT measured immediately afterwards, all on one sample. The experiments are then repeated on different samples, and they show that $\log \sigma$, $\log R$, and dE/dT are linear functions of $1/T$, where T is the mean absolute temperature of the specimen. The graphs for $\log \sigma$ and $\log |R|$ against $1/T$ each consist of two rectilinear portions, one covering the high, the other the low temperature results. Thermo-electric measurements yielded results only for the high temperature part.

The theory of impurity semiconductors is developed and found adequate to explain the variation, at any rate at higher temperatures. It is found that an activation energy of about 2 ev. at high temperatures, and from 0·3 to 0·64 ev. at low temperatures, is required for excitation of electrons to the conduction band. The concentration of impurity centres operative in the high temperature range is about $8{\cdot}6 \times 10^{20}$, the electrons having a mean free path of about 10^{-6} cm. The concentration of free " carriers " varies from 10^{11} to 10^{13} as the temperature rises. NiO behaves like a defect semiconductor, " hole " conduction predominating. The significance of these results is discussed.

§1. INTRODUCTION

Experiments on semiconductors are generally designed either to study the common characteristics of a whole group of materials or else to probe in detail the behaviour of a single substance—or even of a single specimen. The virtue of the second method, of which our work is an example, is the elimination of at least some of the confusing complications which befog the study of the electrical properties of solids, particularly of semiconductors. Small differences of impurity content or heat treatment of different samples of the same material, or obscure differences in the structure of different substances believed to be of the same type, make generalization difficult. If, however, simultaneous measurements of electrical conductivity and Hall effect, or of conductivity and thermo-electric power, are made on one sample, quite definite conclusions can often be arrived at about the internal behaviour of a sample, and thus a good deal of light can sometimes be thrown on the general theory of solids.

In nickel oxide we have selected a substance which seems specially well adapted to this kind of detailed study. Hitherto most work on semiconductors—of which NiO is an example—has been performed on samples of compressed powders, although a few investigations have been carried out with single crystals, e.g. SiC (Busch and Labhardt 1946), or with coherent specimens, as in Cu_2O, formed by oxidizing a strip of copper (Mönch 1933). One of our reasons for choosing NiO was the possibility of forming a suitable specimen by direct oxidation of the metal, thus avoiding, it may be hoped, some of the objections which may be urged against the use of powders. A second reason was the special interest attaching to the ionic structure of solid NiO. It is known that in the crystal lattice the Ni^{++} ions have an incomplete 3d electron-shell, and this suggests the

possibility of free electron movement which might be expected to produce metallic conduction. NiO, however, is by no means a metallic conductor. This interesting dilemma is found in certain other substances in which the 3d shell is incomplete, and de Boer and Verwey (1937) have proposed a theory of these materials. We refer later to the bearing of this theory on our results.

Some measurements of electrical conductivity σ of NiO at different temperatures are already available in the work of Baumbach and Wagner (1934), and the effect on σ and dE/dt (the thermo-electric power) of changes in the pressure of oxygen in the surrounding atmosphere has been measured by Hogarth (1948) in this laboratory with specimens of compressed powders, but no detailed simultaneous study of more than one of the properties is known to us.

§ 2. PREPARATION OF THE SPECIMEN

From the purest obtainable nickel foil a strip of dimensions $7 \times 1{\cdot}1 \times 0{\cdot}0067$ cm. was cut. According to the suppliers, the impurities in this material consisted of traces of Fe, Cu, Mn, Co, to a total of 0·4%. The strip was first rolled flat and two small holes were made, one near each end. From these holes the strip was suspended under tension along the axis of a vertical tube furnace so that a current of air flowed constantly past the specimen and the strip was prevented from buckling. While in this position it was maintained at a temperature of

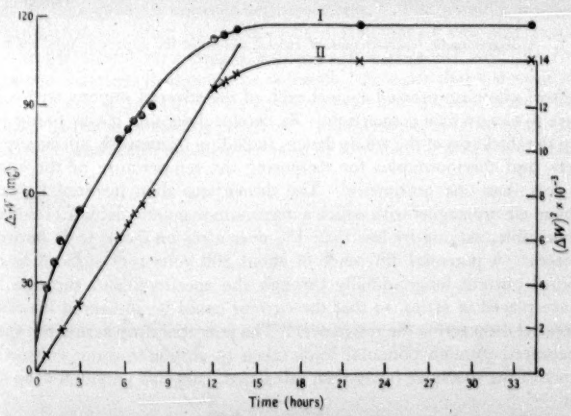


Figure 1. Increase in weight of the specimen due to oxidation as a function of the time.
Curve I shows the increase in weight as a function of the time.
Curve II shows the square of the increase in weight as a function of the time.

1,000° c. for a period up to 30 hours, after which oxidation was considered to be complete. For our investigation it is naturally most important that we should be sure of the completeness of the oxidation, and to this end one specimen was removed from the furnace from time to time and weighed. Figure 1 shows how the weight increased, the constancy after about 20 hours indicating completion. (The observations show that the square of the gain in weight is proportional to the time, as curve II of Figure 1 illustrates.) Examination of the broken section after about 30 hours' heating revealed no sign of unoxidized core.

Upon this very fragile specimen it was next necessary to prepare electrical contacts. These were made by evaporating silver *in vacuo* on to the specimen over the small regions required, namely one region at each end for the entrance and exit of the main current and for the attachment of potential leads, and another pair at the middle of the two long edges for the attachment of the Hall effect electrodes.

§3. APPARATUS FOR HALL EFFECT AND CONDUCTIVITY, AND METHOD OF MEASUREMENT

The strip specimen prepared in this manner was mounted, together with a heating element of nichrome ribbon, as illustrated in Figure 2, within a framework of "syndanio" or asbestos slate, the heater being carefully insulated from the specimen by means of mica. When the framework was assembled, spring

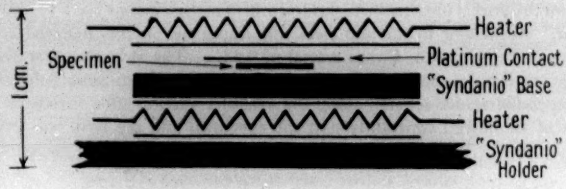


Figure 2. A diagrammatic representation of an end section of the apparatus used for measuring the Hall effect and conductivity.

contacts of platinum pressed against each of the silvered regions with sufficient pressure to ensure firm connection. By careful designing it was found possible to keep the thickness of the whole device, including framework, specimen, heater, contacts, and thermocouples for measuring the temperature of the specimen, rather less than one centimetre. The device was then inserted between the poles of an electromagnet with which a maximum magnetic field of 11,500 oersted was obtainable, varying by less than 1% over a region 3 cm. wide between the pole-pieces. A potential difference of about 500 volts D.C. sufficed to drive a very small current longitudinally through the specimen and through a fixed resistance placed in series, so that the current could be measured by observing the potential drop across the resistance. The potential drop across the specimen was measured through potential leads taken to an electrostatic voltmeter, the resistance of the specimen being then calculated from this potential drop and the current.

The resistance was measured in this manner after air currents had been excluded from the apparatus as far as possible, and after sufficient time had elapsed to ensure thermal equilibrium; the Hall effect was then measured. For this purpose the lateral contacts were connected, via a quadrant electrometer or sensitive galvanometer, to a thermocouple-type potentiometer, the magnetic field was switched on, and the transverse potential difference between the Hall electrodes balanced out. This potential difference is generally the sum of two parts, due respectively to the Hall effect and to the small departure from exact symmetry which it is generally impossible to avoid in placing the Hall electrodes. If the magnetic field is now reversed, the contribution from the Hall effect is reversed, while the other contribution remains unaffected. The difference between the readings of the potentiometer is then twice the Hall E.M.F.

§4. ARRANGEMENT FOR THERMO-ELECTRIC EFFECT

For measurement of the thermo-electric effect the specimen in its framework was removed from the magnet after the completion of the conductivity and Hall effect measurements, and arranged in an electric furnace so that the temperature of one of its ends differed by 40° or 50° C. from that of the other, the greatest care being taken to exclude draughts, which are liable to set up uncontrollable temperature fluctuations. Experiments making use of larger and of smaller temperature differences were found to lead to practically the same results. Against the two ends were pressed pieces of platinum to form the hot and cold junctions, and the thermo-E.M.F. was measured with the potentiometer, using a sensitive galvanometer as indicator at higher temperatures, and a quadrant electrometer at low temperatures. The temperatures of the ends were measured with the aid of thermocouples, and the mean temperature T used as the temperature of the specimen in plotting the results. Below 300° C. mean temperature the results were erratic, probably because of a distinct thermo-electric effect in the syndanio holder.

§5. RESULTS

Preliminary experiments were first performed to verify that the conduction was completely electronic. Ohm's law was found to be obeyed over the range of currents used. Moreover, supplementary experiments designed to detect any transport of ions gave an entirely negative result. The possible interference of the Ettingshausen effect on the measured Hall E.M.F.S was also examined. No measurable lateral temperature difference that reversed with the reversal of the applied magnetic field could be detected. In order that E.M.F.S of magnitude similar to that of the Hall E.M.F.S should be produced, a temperature difference of the order of 100° C. would be required. Furthermore, reversal of the applied magnetic field produced immediate reversal of the lateral E.M.F., which remained

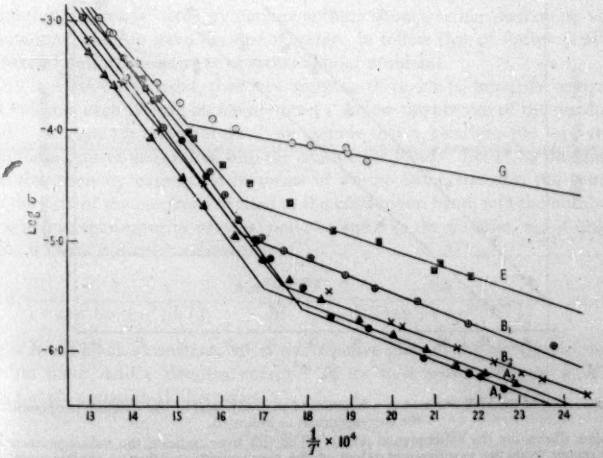


Figure 3. Log of the conductivity as a function of the reciprocal of the absolute temperature for various specimens as indicated.

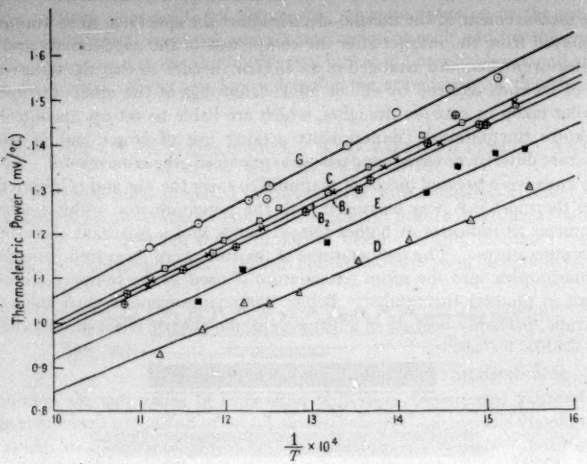


Figure 4. The thermo-electric power as a function of the reciprocal of the absolute temperature for various specimens as indicated.

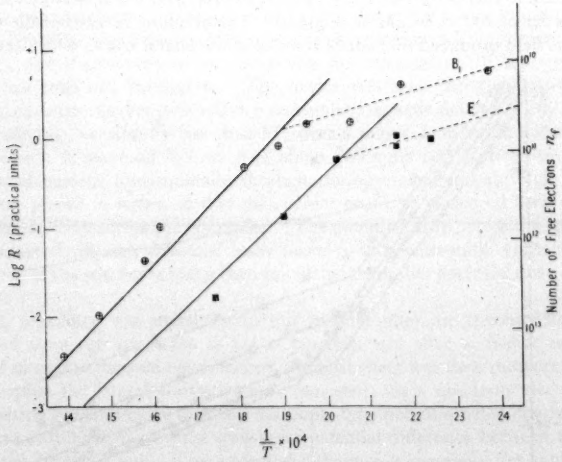


Figure 5. Log of the Hall constant as a function of the reciprocal of the absolute temperature for the two specimens as indicated.

The points shown are the experimental points. The full lines indicate the values predicted by the theory from the experimental values of the conductivity and thermo-electric power.

constant thereafter. We considered, therefore, that the contribution due to the Ettingshausen effect must have been less than 1% of the total E.M.F. measured.

Experiments were carried out on many specimens, but because of their extreme fragility several failed to survive for the complete series of observations. In the graphs of Figures 3, 4 and 5 results for different samples are indicated by letters. Thus B, for example, indicates the simultaneous results for conductivity σ and Hall effect R, and for the subsequent measurements of thermo-electric power dE/dT, made on the same sample. For reasons discussed in the next section, the abscissae in all the graphs are in units of $10^4/T$, where T is the mean temperature of the specimen, so that high temperature results appear to the left of the diagrams. It will be seen that when $\log\sigma$, $\log R$, or dE/dT is plotted as ordinate, the results appear to lie on sets of straight lines, and the reasons for this regularity will now be discussed.

§ 6. THEORY

We suppose that the chief energy levels in the semiconductor consist of a lower band completely filled with electrons at absolute zero of temperature, together with a higher band completely empty at absolute zero, the two bands being separated by a forbidden energy step, in which no energy levels exist except for a narrow range of levels due to the presence of impurities. If the semiconductor is of the "excess" or "normal" type, these impurity levels are to be found near the bottom of the upper or conduction band, and at absolute zero are considered to be completely filled with electrons. In a "defect" or "abnormal" semiconductor, the impurity levels are near the top of the lower filled band, and are considered to be empty at absolute zero. With minor changes the theory is the same in both cases, and it is customary to develop it for excess semiconductors. In what follows this procedure is adhered to. Developments of the theory already made by various authors show a rather distressing variety of notations, and we have decided therefore to follow that of Putley (1949) for the sake of uniform treatment of rather similar problems.

As in Putley's account, then, we suppose there are n_b impurity centres per unit volume, each having an energy level ϵ' below the bottom of the conduction band. At absolute temperature T we assume that n_i electrons per unit volume from these centres are excited into the conduction band. Let ϵ^* be the chemical potential, then by expressing in terms of Fermi–Dirac statistics the condition that the sum of the electrons excited to the conduction band, and the number left unexcited in the impurity centres, must be equal to the number, n_b, of impurity levels, it is not difficult to show that

$$n_b \frac{1}{1+\exp\{(\epsilon'+\epsilon^*)/\boldsymbol{k}T\}} = \frac{4\pi(2m^*)^{3/2}}{\boldsymbol{h}^3}\int_0^\infty \frac{\epsilon^{\frac{1}{2}}d\epsilon}{1+\exp\{(\epsilon-\epsilon^*)/\boldsymbol{k}T\}}, \quad \ldots\ldots(1)$$

where $\boldsymbol{h}$ is Planck's constant, m^* is the effective mass of the electron in the conduction band, and ϵ denotes energy. It we now write $\epsilon/\boldsymbol{k}T=\eta$, $\epsilon'/\boldsymbol{k}T=\eta'$, $\epsilon^*/kT=\eta^*$, equation (1) becomes

$$n_b \frac{1}{1+\exp(\eta'+\eta^*)} = \frac{4\pi(2m^*\boldsymbol{k}T)^{3/2}}{\boldsymbol{h}^3}\int_0^\infty \frac{\eta^{\frac{1}{2}}d\eta}{1+\exp(\eta-\eta^*)}. \quad \ldots\ldots(2)$$

In the same notation n_f is given by

$$n_f = \frac{4\pi(2m^*kT)^{3/2}}{h^3}\int_0^\infty \frac{\eta^{\frac{1}{2}}d\eta}{1+\exp(\eta-\eta^*)}. \qquad \ldots\ldots (3)$$

In these expressions the reduced chemical potential η^*, which is a function of the concentration of electrons, may be considered as a parameter indicating the degree of degeneracy of the electron gas—a device used extensively by Shifrin (1944). Now Shifrin has shown that if $n_f < 10^{18\cdot5}$, so that the degree of degeneracy is very small, and $-\eta^* \gg 1$, then to an accuracy of better than 5%, we may write

$$\tfrac{1}{2}\int_0^\infty \frac{\eta^{\frac{1}{2}}d\eta}{1+\exp(\eta-\eta^*)} = \frac{\sqrt{\pi}}{4}\exp\eta^*.$$

We shall present evidence to show that in NiO the concentration of charge carriers is probably very much less than $10^{18\cdot5}$ per cm^3, so that the approximation may be used with confidence in our case, and we may write $n_f = K\exp\eta^*$, where $K = 2(2\pi m^* kT/h^2)^{3/2}$, and it then follows from equation (2) that

$$n_b = n_f + K\exp(\eta' + 2\eta^*).$$

If the number of carriers excited is only a very small fraction of n_b, as it appears to be in NiO, the second of these equations may be written approximately as

$$n_b = K\exp(\eta' + 2\eta^*),$$

so that
$$n_f = \sqrt{(Kn_b)}\exp(-\eta'/2),$$

and
$$\eta^* = \ln n_f/K = \ln\sqrt{(n_b/K)} - \eta'/2.$$

The expressions for the Hall effect R, conductivity σ and thermo-electric effect dE/dT, derived by several authors (see Seitz 1940, p. 192) for this model, may now be expressed as follows:

$R = \pm 3\pi/8n_f e$, where e is the electronic charge in E.M.U. Hence

$$\ln|R| = \ln\{3\pi/8e\sqrt{(n_b K)}\} + \epsilon'/2kT.$$

$\sigma = 4n_f l_0 e^2/3\sqrt{(2m^*\pi kT)}$, where the mean free path l_0 of electrons is assumed to be constant over the relevant range of electron energies.

$$\ln\sigma = \ln\left[\sqrt{n_b}l_0\frac{4}{3}e^2\sqrt{\left(\frac{K^2}{2\pi m^* kT}\right)}\right] - \frac{\epsilon'}{2kT},$$

$$dE/dT = \pm\frac{k}{e}(2-\eta^*) = \pm\frac{k}{e}\left(2-\ln\sqrt{\left(\frac{n_b}{K}\right)} + \frac{\epsilon'}{2kT}\right) \dagger$$

In these expressions the main variation with temperature is due to the term $\epsilon'/2kT$, and over the range of temperature used in our experiments the deviation from constancy of the remaining terms is small and produces a negligibly small change in the value of the whole expression. Consequently $\log|R|$, $\log\sigma$ and $|dE/dT|$ all differ from linear functions of $1/T$ by negligible amounts. It follows that from the gradients and intercepts of appropriate graphs n_b, ϵ' and l_0 may all be found. From n_b and ϵ' a value of η^* can be calculated, and hence n_f. It is of course implied that the values of R, σ and dE/dT used in this computation should have been measured simultaneously on the same specimen.

† Seitz (1940, p. 191) gives a formula for the Thomson coefficient from which our formula may be derived.

In order to facilitate the calculation, numerical values of k, e etc. may be inserted—taking m^* to be the electronic mass and $T = 625°$ A. in the nearly constant term of the expression for σ. We then have

$$\log|R| = \frac{\epsilon'}{3{\cdot}96}\frac{10^4}{T} - \log\sqrt{n_b} + 0{\cdot}9325,$$

$$\log\sigma = -\frac{\epsilon'}{3{\cdot}96}\frac{10^4}{T} + \log(l_0 n_b^{\frac{1}{2}}) - 0{\cdot}948,$$

$$|dE/dT| = \frac{\epsilon'}{2}\frac{10^4}{T} + \frac{1}{11{\cdot}7}(24{\cdot}78 - \ln\sqrt{n_b}) \quad \text{mv/deg.}$$

Making use of these equations, the constants shown in the Table are obtained for the different specimens. In this list B_1 and B_2 refer to a single sample in which the conductivity and Hall effect are first determined as usual (B_1), then the thermo-electric power is measured, and finally the conductivity is measured a second time (B_2). The small difference between these two sets of results is no doubt due to the intervening heat treatment. In most of the specimens the most elusive quantity was R, the Hall effect. In most cases the true Hall E.M.F. was obscured by sudden and uncontrollable fluctuations, which may, perhaps, have been caused by imperfections in the necessarily delicate contacts, but which generally could not

Specimen	Conductivity measurements High temp.		Low temp.		Thermo-electric measurements High temp.		
	(1)	(2)	(3)	(4)	(5)	(6)	(7)
A_1	2·16	4·90	0·61	−1·91			$3{\cdot}4 \times 10^{-6}$
A_2	2·09	4·65	0·61	−1·85			$1{\cdot}9 \times 10^{-6}$
B_1	2·15	4·75	0·64	−1·18	1·84	20·7	$2{\cdot}4 \times 10^{-6}$
B_2	2·04	4·42	0·64	−1·94	1·85	20·7	$1{\cdot}12 \times 10^{-6}$
C					1·86	20·6	
D					1·67	20·9	
E	1·88	4·10	0·52	−1·49	1·74	20·8	$0{\cdot}54 \times 10^{-6}$
G	1·92	4·48	0·30	−1·85	1·94	20·7	$1{\cdot}3 \times 10^{-6}$

(1), (3), (5) ϵ' (ev.); (2), (4) $\log(l_0\sqrt{n_b})$; (6) $\log n_b$; (7) calculated values of l_0 ($n_b = 5{\cdot}37 \times 10^{20}$).

be eliminated. In two samples only (B and E) steady results were consistently obtained, and these are shown in Figure 5. At the lower temperatures, measurements of thermo-electric power were also found difficult to make with any degree of certainty, and we therefore include only the much more dependable results obtained at temperatures above 370° C. Now it will be observed from the diagrams that the graphs of $\log\sigma$ and $\log R$ each consists of two straight lines, a low temperature and a high temperature section. The results we give for dE/dT correspond only to the high temperature parts of the other graphs. It may be that a determination of dE/dT at low temperatures will eventually show a similar division of results into two parts, at high and low temperatures, but at present our low temperature results would not justify a definite statement about it.

In these results it is worth noticing that the figures obtained from the thermo-electric measurements agree rather better among themselves than do the conductivity results.* In particular the satisfactory constancy of $\log n_b$, as calculated

* The values for ϵ' obtained from the conductivity measurements are in good agreement with those obtained by Baumbach and Wagner (1934). Their results, however, showed no special low temperature region. This probably indicates that their specimens were freer from foreign impurities.

from these measurements justifies the use of the mean value of $\log n_b$ in the calculation of the mean free path from the values of $\log l_0\sqrt{n_b}$ in the third (high temperature) column of the Table. Results for l_0, calculated in this way, are shown in the last column of the Table, and indicate an extreme variation of mean free path of about 5 to 1 between the specimens. The order of magnitude of l_0 (10^{-6} cm.) does not appear to be unreasonably large—it compares well, for example, with the mean free path estimated for cuprous oxide (Mott and Gurney 1940, p. 168).

We are now in a position to see how far the Hall effect results fall into line with the others. From values of ϵ' and n_b, $\log|R|$ at any temperature can be calculated from the formula already quoted. For the low temperature range we have no independent value of n_b, but over the high temperature region we have the values of $\log n_b$ given in the Table. For the same range we have also two separate values of ϵ' for each specimen, and we have taken the mean of these in calculating R. In Figure 5, showing the variation of $\log R$, the continuous line passes through points calculated in this manner. The agreement therefore seems to be very satisfactory. Moreover, since $R=(3\pi/8en_f)$, the numbers of free carriers in the two specimens may now be calculated at different temperatures. These numbers are given on the right-hand scale of Figure 5, and are seen to vary between about 10^{11} and 10^{13} per cm^3 over the high temperature range. The average number of impurity centres, n_b, is about $8{\cdot}6\times10^{20}$ per cm^3.

In the thermo-electric experiments the cold end of the specimen was positive, as would be expected if the carriers were positively charged. This indicates that conduction takes place by "positive holes"—or in other words that NiO is a defect or "abnormal" semiconductor, and this was confirmed by the direction of the Hall E.M.F.

§7. DISCUSSION

It seems quite clear from these results that in the higher temperature range NiO is an impurity semiconductor of the kind already considered in the theory. It may be presumed that through the low temperature range the main action is of the same character, but that at these temperatures the contribution due to those impurity centres which are active at high temperatures is small, another set of impurity centres with lower activation energy then dominating the action. At this point the experiments of Jusé and Kurtschatow (1932) on cuprous oxide may be recalled. Their results for conductivity bear a striking resemblance to ours for NiO, and for the high temperature parts of their graphs they offer the suggestion of intrinsic conduction, that is, the conduction is supposed to be due to the direct excitation of electrons from the lower band of energy levels (supposed all filled at $T=0$) to the conduction band. Since the transference of an electron in this fashion creates at the same time a positive hole in the lower band, conduction must be due to the combined effect of free electron and free hole. The theory of conduction differs in this case from ours. Some aspects of it have been worked out by Fowler (1933). It is easy to see that changes introduced by a theory of intrinsic conduction would differ according to the electrical property being considered. Thus changes in the predicted variations of Hall effect and thermo-electric power, which depend on the first power of the carrier charge, would be very unlikely to resemble the changes in the variation of conductivity, which depends on the second power of the charge. The convincing agreement of the

results for σ and dE/dT with those for R in NiO, as interpreted by the theory of impurity conduction, seems to show that intrinsic conduction cannot play the main, or even an important, part in our experiments.

On the nature of the impurity centres evidence at present is not conclusive. From experiments in this laboratory Hogarth has shown that the thermo-electric power of NiO is a linear function of log P_0, where P_0 is the pressure of oxygen in the surrounding atmosphere. On certain hypotheses it is possible to account for this kind of variation in terms of the quasi-chemical equilibrium of oxygen in the crystal lattice, but reasonable assumptions about the underlying mechanism do not seem to lead to good numerical agreement when the variation is calculated. It is, however, generally assumed that the extra oxygen absorbed is to be found in correct lattice positions, so that a number of vacant Ni sites remain. If we take the crystal density of NiO to be 7·45 gm/cm^3, unit volume will contain about $6{\cdot}9 \times 10^{22}$ atoms of Ni or of O, the total number of atoms of both kinds being therefore about $1{\cdot}38 \times 10^{23}$ per cm^3. The $8{\cdot}6 \times 10^{20}$ impurity centres per cm^3 therefore represent about 0·62 atomic per cent. This is also generally considered to be about the percentage of excess oxygen in black NiO obtained by oxidizing green-grey NiO. Our specimens, although dark, were not black, however. While it may be assumed that the impurities in the higher temperature range are due to this excess oxygen, there still remains the problem of the centres of lower activation energy which predominate at low temperatures. In one particular the hypothesis introduced by de Boer and Verwey, primarily to explain the lack of metallic conduction in NiO, finds some corroboration in our results. This is the existence of an internal potential barrier requiring an activation energy of about 2 ev. to surmount. We do in fact find an activation energy of that magnitude (see Table).

ACKNOWLEDGMENTS

We should like to express our gratitude to Professor H. R. Robinson, in whose laboratory these experiments were performed, for facilities and advice. The work was carried out with the assistance of a grant from the Department of Scientific and Industrial Research.

REFERENCES

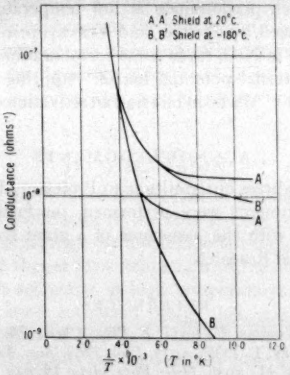
Baumbach, H. H., and Wagner, C., 1934, *Z. Phys. Chem.*, **24**, 59.
de Boer, J. H., and Verwey, E. J. W., 1937, *Proc. Phys. Soc.*, **49**, extra part, 59.
Busch, G., and Labhardt, H., 1946, *Helv. Phys. Acta*, **19**, 643.
Fowler, R. H., 1933, *Proc. Roy. Soc.* A, **141**, 56.
Hogarth, C. A., 1948, *Thesis*, London.
Jusé, W., and Kurtschatow, B. W., 1932, *Phys. Z. Sowjet*, **2**, 453.
Mönch, G., 1933, *Z. Phys.*, **83**, 247.
Mott, N. F., and Gurney, R. W., 1940, *Electronic Processes in Ionic Crystals* (Oxford : University Press), p. 168.
Putley, E. H., 1949, *Proc. Phys. Soc.* A, **62**, 284.
Seitz, F., 1940, *Modern Theory of Solids* (New York and London : McGraw-Hill Book Co., Inc.).
Shifrin, K., 1944, *J. Phys., U.S.S.R.*, **8**, 242.

LETTERS TO THE EDITOR

Increased Sensitivity of Infra-red Photoconductive Receivers

A number of investigators have observed the anomalous dependence on temperature of the conductance of infra-red sensitive photoconductive films. The conductance is found to decrease rapidly on first lowering the temperature, whereas, on further cooling, the conductance tends to a steady state or may even increase again. Several hypotheses regarding the constitution of the layer (Macfarlane 1948) have been advanced to account for this behaviour; however, Simpson (1948) recently demonstrated that for films of lead telluride, with photosensitivity at wavelengths up to 5·5 μ, this effect may be attributed entirely to radiation from the surroundings falling on the photoconductive surface. It has now been shown, firstly, that the same explanation holds for films of lead sulphide sensitive only up to 3·8 μ, and secondly, that by removal of this background irradiation a large increase in sensitivity can be obtained.

In the present investigation a highly sensitive chemical type lead sulphide cell, B.T.H. type C, in the form of a small Dewar flask, was completely enclosed in a metal shield. On immersion in liquid air, the case cooled immediately to −183° c., while the sensitive surface took about 20 minutes to reach this temperature. This allowed the conductivity of the layer to be determined at various temperatures, the shield being maintained at liquid air temperature. Similarly, by allowing liquid air to evaporate completely from the inside of the Dewar flask, the film slowly warmed and conductivity measurements were made over the same temperature range, the shield being maintained at room temperature. These results are shown in curves A and B of the Figure, where the logarithm of the conductance is



plotted against the reciprocal of the absolute temperature. It will be seen that the effect of excluding the room temperature radiation is to produce a continuous decrease in conductance with decrease in temperature.

If a small constant amount of radiation is allowed to fall on the sensitive surface through a small aperture in the shield, curve A is displaced to A′ and curve B to B′. Defining sensitivity as $(\sigma_I - \sigma_D)/\sigma_D$ where σ_D and σ_I are the conductivities of the layer in the dark and when irradiated, respectively, the vertical interval between the curves A and A′, or B and B′ is a measure of the sensitivity. It will be observed that the exclusion of the background room temperature irradiation greatly increases the sensitivity of strongly cooled layers.

Modern techniques, using modulated radiation, have made the signal-to-noise ratio of far greater importance than the sensitivity as defined above. It is well known that the signal-to-noise ratio of chemically deposited lead sulphide cells can be increased by a factor of 10 by cooling to −80° c. On further cooling to liquid air temperatures the improvement for the higher sensitivity cells is, however, small; in some cases even a deterioration of signal-to-noise ratio occurs. It has now been found that if the sensitive layer is shielded from the

constant irradiation of its surroundings, the signal-to-noise ratio increases continuously with decrease in temperature. By cooling the cell with liquid air and maintaining the shield at the same temperature, both the resistance and the signal-to-noise ratio are increased to over 1,000 times their value at room temperature. Measurements have demonstrated a detection limit of 2×10^{-8} watt.cm^{-2} for 85° c. black-body radiation, and 2×10^{-13} watt.cm^{-2} at the peak of its spectral response for 1 c/s. bandwidth.

If full advantage is to be taken of this greatly increased sensitivity, great care must be exercised in the design of the first stage of the amplifier. The high values of the resistance reached by these cells, when cooled and shielded, may well require the use of an electrometer type of valve in the pre-amplifier. It has been widely recognized that the response time of this type of cell increases with resistance; in the case illustrated above, the time constant increased from about 40 microseconds at room temperature to a value of 10–20 milliseconds when the cell was cooled and screened at liquid air temperatures. Therefore it is necessary to use much lower interruption frequencies than those normally employed with this type of receiver. The above measurements were made with an interruption frequency of $16\frac{2}{3}$ c/s.

It was considered possible that the increase in sensitivity might be accompanied by an extension of the spectral response curve to longer wavelengths, similar to that already found on cooling (Moss 1947). However, preliminary spectral response measurements do not indicate any such extension. It can be shown that loss of the maximum sensitivity is not solely associated with long wavelengths (room-temperature radiation). When the resistance of a cooled and shielded cell was reduced to a similar extent by a constant irradiation at short wavelengths (tungsten lamp), the signal-to-noise ratio for a small superimposed modulated irradiation was also greatly reduced.

I desire to thank Mr. L. J. Davies, Director of Research, The British Thomson-Houston Co. Ltd., for permission to publish this note, and Dr. C. J. Milner for many helpful discussions.

British Thomson-Houston Co. Ltd.,
Rugby.
14th May 1949.

B. N. Watts.

Macfarlane, G. G., 1948, *M.I.T. Conference on Physical Electronics*, April 1948.
Moss, T. S., 1947, *Nature Lond.*, **159**, 476.
Simpson, O., 1948, *Proc. Phys. Soc.*, **61**, 487.

The Decay Constant of Radio-Sodium, ^{24}Na

The accurate determination of decay constants is a tedious measurement not altogether free from the danger of systematic errors which can be troublesome to detect and eliminate For this reason the number of radioactive substances for which the decay constant is known with precision is quite small, careful measurements usually being made only when an accurate value is required for a special purpose.

During the course of some work using radio-sodium as a calibrated source of monochromatic γ-rays, the decay constant was redetermined with the object of enabling accurate estimates of the activity to be made, even after the lapse of several half periods. A good knowledge of the decay constant was essential as the absolute determination * of the activity of the radio-sodium could only be made on an aliquot fraction some considerable time after the irradiated sodium carbonate had been withdrawn from the pile.

The method adopted was to measure the ionization produced by the γ-radiation in a large shallow chamber 50 cm. diameter and 6 cm. total depth. The source was placed on a stand 6 cm. above the chamber. The advantage of a chamber of this type, which is similar to that used by Madame Curie (1912) in her work on the γ-rays of radium, is that errors due to location of the source are quite negligible. The ionization current was compared directly with that produced by a 200 mc. radio-thorium standard. This eliminates, or greatly reduces, the two main sources of error in work of this type, namely, changes

* The absolute determination was made by J. L. Putman and R. Wilment at A.E.R.E., Harwell using a β–γ coincidence method.

in the sensitivity of the electrometer and changes in the efficiency of the chamber such as are due to changes in barometric pressure and humidity. The time was measured to the nearest 10 seconds with a chronometer which had been compared with the laboratory crystal-controlled clock.

The ionization currents were compared using a selected 954 valve as an electrometer valve.

The circuit used is shown in Figure 1. The electrometer is used only as a null instrument, the measurement consisting of a comparison of the voltage produced by the ionization current passing down a fixed grid resistance R† with that obtained with a low-voltage potentiometer. The method is alternative to that described by Ward (1939), and enables quicker measurements to be made with strong sources.

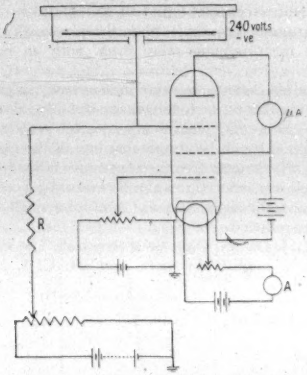


Figure 1. Circuit diagram of ionization chamber and electrometer valve. Resistance R is 10,000 megohms.

It was found that in this way the two sources could be compared accurately with a time interval of only a few minutes between the measurements, thus greatly reducing errors due to drift in the characteristic of the electrometer valve and grid leak.

The results obtained are shown in the Table.

Series I		Series II		Series III	
Time (hours)	Resistance ratio	Time (hours)	Resistance ratio	Time (hours)	Resistance ratio
0	3·75139	0	2·43170	0	3·60647
6·51667	5·04451	2·96667	2·81181	0·21667	3·59673
19·05000	8·93435	6·25000	3·27573	2·76667	4·12194
22·70000	10·72052	10·63333	4·01195	2·95000	4·11092
27·41667	13·34078	22·30000	6·88563	6·90000	4·94828
42·70000	27·43638	27·30000	8·68861	6·96667	4·93040
44·16667	29·26085	29·90000	9·85738	18·91667	8·62175
				19·03333	8·64929
				23·36667	10·56491
				23·43333	10·20523
				27·05000	12·57298
				27·16667	12·52778

† For Series I an S.S. White resistor was used, and for Series II and III a Welwyn resistor.

The decay constant was calculated from the linear logarithmic plot (Figure 2) by Gauss' method of least squares. This assumes that all the readings have equal weight, but this is not the case since the experimental quantities which may be assumed to have equal weights are the actual ionization currents.

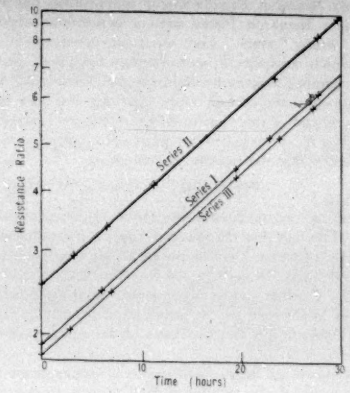


Figure 2. Linear logarithmic plot of resistance ratio against time in hours. For series I and III the ordinate is divided by 2.

Thus, if the activity A has an error ϵ so that the ionization current is $(A\pm\epsilon)=A(1\pm\epsilon/A)$, then the ordinate y in the logarithmic plot is given by $y=\log A+\log(1\pm\epsilon/A)=\log A\pm\epsilon/A$. Thus the points on the logarithmic plot must be weighted according to the square of the measured activity. The results obtained from the three series of measurements are as follows. A correction was made for the decay of the radio-thorium source.

Series I	$14{\cdot}8878\pm0{\cdot}02$ hrs.	$(14{\cdot}89\pm0{\cdot}03)$
Series II	$14{\cdot}8952\pm0{\cdot}02$ hrs.	$(14{\cdot}89\pm0{\cdot}036)$
Series III	$14{\cdot}9170\pm0{\cdot}03$ hrs.	$(14{\cdot}94\pm0{\cdot}038)$

Average $=14{\cdot}90\pm0{\cdot}02$ hrs.
Decay constant $=0{\cdot}04652\pm0{\cdot}000062$ hr^{-1}.

The figures in brackets are those obtained by a simple graphical treatment in which the slope is calculated from every combination of these points and the average taken. The mean value stated lies within the limits of error quoted by van Voorhis (1936). The three decay constants calculated by Gauss' method agree within the estimated error. The small differences from the value (in brackets) obtained graphically from the logarithmic plot shows that the observed ionizations are well represented throughout the measurement by an exponential decay, so that there is no reason to suppose that any errors due to changes in the high resistance units have not been eliminated.

We have to thank A.E.R.E., Harwell, for the radioactive sodium and Messrs. Putman and Wilment for work on this, the Department of Scientific and Industrial Research for maintenance grants, and Mr. C. H. Collie for his interest and advice.

Clarendon Laboratory,
Oxford.
23rd February 1949.

R. Wilson.
G. R. Bishop.

Curie, E., 1912, *J. Phys. Radium*, **2**, 795.
van Voorhis, S. N., 1936, *Phys. Rev.*, **49**, 889 A.
Ward, A. G., 1939, *Proc. Camb. Phil. Soc.*, **35**, 523.

The Photo-Disintegration of Oxygen into Four Alpha-Particles

The Atomic Energy Research Establishment synchrotron has been used to irradiate unloaded Ilford Nuclear Research Plates with a continuous spectrum of gamma-rays extending to 23 MeV. Many " stars " were observed, consisting of three or four charged particles, in some of which unobserved neutrons may have been present; such stars were expected from cloud-chamber studies by Baldwin and Klaiber (1946). Among the stars observed, thirteen have consisted of four alpha-particles and may be identified as oxygen disintegrating. A typical star of this type is shown in Figure 1 (see Plate), and a histogram showing the total energy, E_T, released in the four alpha-particles of each star is shown in Figure 2. If it is assumed that the reaction occurring is

$$^{16}O = 4\,^4He + 14{\cdot}6 \text{ MeV.}, \qquad \ldots\ldots (1)$$

then a scale of the energy, E_γ, of the gamma-ray producing a particular star may be added as shown (upper scale). The fact that the spectral limit of the radiation and the limit of the energy released differ by 14·6 MeV. (within the limits to which the spectral limit has been determined, namely, $\pm 0{\cdot}5$ MeV.) is perhaps the surest indication that the reaction occurring is that of equation (1). Further evidence, and also an indication that neutrons are not involved in the reaction, is afforded by the momentum balance in the stars. The balance agrees with equation (1), assuming that the range of the alpha-tracks may be subject to an error of $0{\cdot}5\,\mu$.

The number of stars observed is too small to give evidence of the detailed mechanism of equation (1) by an analysis of the distribution of energy amongst the individual alpha particles. It is unlikely, from the work of Hänni *et al.* (1948) on the disintegration of carbon that oxygen would disintegrate directly into four alpha-particles; more probably the disintegration will involve an excited level of ^8Be as an intermediate stage (with or without ^{12}C as a further intermediary). Such mechanisms would be consistent with the form of the stars observed and would also account for the fact that no small stars (with E_T less than 6 MeV.) have been detected.

The cross section of the reaction may be estimated from the known composition of the plate, a measurement of the ionization produced in a chamber with thick graphite walls, and a spectrum calculated theoretically (Heitler 1944). The mean value of the cross section thus obtained, for quanta between 20·5 and 23 MeV., is 2×10^{-29} cm^2; this value may be in error by a factor of two, due to deviations of the spectrum from the theoretical value, particularly near the threshold, and also due to poor statistics.

This letter is published with the approval of the Director of the Atomic Energy Research Establishment.

Atomic Energy Research Establishment,
Harwell, Didcot, Berks.
25th May 1949.

F. K. Goward,
E. W. Titterton,
J. J. Wilkins.

Baldwin, G. C., and Klaiber, G. S., 1946, *Phys. Rev.*, **70**, 259.
Hänni, H., Telegdi, V. L., and Zunti, W., 1948, *Helv. Phys. Acta*, **21**, 203. (Several hundred carbon disintegrations have also been observed in plates irradiated by the synchrotron, and are being analysed at A.E.R.E. and at E.T.H., Zürich.)
Heitler, W., 1944, *Quantum Theory of Radiation* (Oxford : University Press).

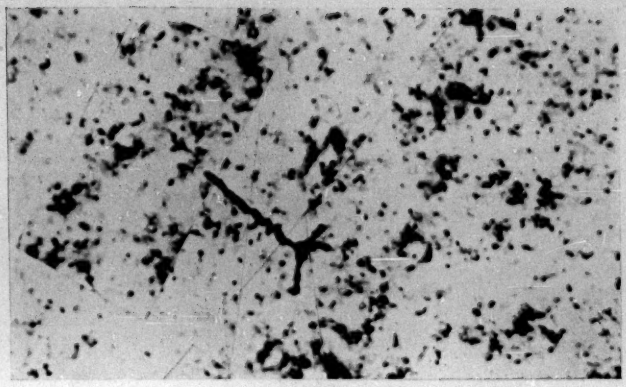


Figure 1. ^{16}O (λ, 4α) Event. Observer Mrs. B. D. Mathieson. Ilford type C_2 Emulsion. The α-particle ranges are 3·3, 3·3, 4·4 and 15·7 μ respectively, representing an energy release of 7·3 MeV.

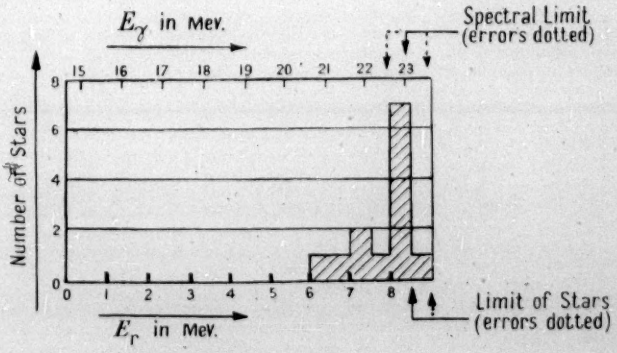


Figure 2. Histogram of oxygen stars.

To face page 460

REVIEWS OF BOOKS

Chambers' Six-figure Mathematical Tables, by L. J. COMRIE. Volume 1, Logarithmic Values, pp. xxii + 576; Volume 2, Natural Values, pp. xxxvi + 576. (Edinburgh and London: W. & R. Chambers Ltd., 1948.) 42*s*. each volume.

Chambers' *Mathematical Tables* is probably the best known set of tables (with the possible exception of the Board of Education's four-figure set), and the present two volumes are in some sense the successor to it, for it appears that in 1944, the centenary of their publication, Dr. Comrie was asked to report on that work with a view to bringing it thoroughly abreast of modern requirements, and that the new work is the outcome.

The bulk of the old book was a 200-page table of seven-figure logarithms and just over 130 pages of natural and logarithmic trigonometric functions; the remainder of its 454 pages were occupied with a miscellany of geodetic and navigational tables. The new work, even if a successor to the old, is in no sense a revision of it. Dr. Comrie has considered first the requirements of the present-day physicist and statistician and provided the tables he is likely to need, to an accuracy which seems adequate for most work. The logarithms are now to six figures, and occupy 180 pages, but data for obtaining eight-figure logarithms are also provided (the old book gave ten figures for argument 1 to 1·06 at intervals of 0·0005).

In volume 2, the more interesting of the two, we have, for $x = 1$ to 1,000, the square, cube and fourth power (fifth power up to 100), the reciprocal, the factorial and the prime factors, as well as $\log x!$ and $x^{\frac{1}{2}}$ $(10x)^{\frac{1}{2}}$, $x^{\frac{1}{3}}$, $(10x)^{\frac{1}{3}}$ and $(100x)^{\frac{1}{3}}$ and some powers of the reciprocals. The factorials above 200 are here published for the first time. From 1,000 to 3,400 we have the square, cube and prime factors. There is also a table of the first 1,540 primes, the largest of which is 12,919; evidently this table is in no sense a competitor with the specialist tables for the use of those interested in properties of numbers. There are three sets of tables of the circular functions, with arguments respectively in degrees and minutes, in radians, and in degrees and decimals of a degree. In each case the cot and cosec for small angles are given at a reduced interval, and the usual auxiliary functions are provided for the functions where they become excessively large. There is a table for conversion from rectangular to polar coordinates.

The hyperbolic functions are well tabulated, as well as natural logarithms, the inverse hyperbolic (and circular) functions and the Gudermannian with its inverse.

Beyond these elementary functions, a selection of transcendents has been made, the choice falling on the gamma function and the probability integral in its two main forms. Here the range has been most carefully considered so that the danger of a user wanting values beyond the arguments tabulated is very small. Where so much is provided it is ungenerous to complain, but I think many a physicist would have welcomed some tabulation of elliptic functions, if only in the form of the elliptic integrals E and F.

This very short account of the volume, which does not do justice to the care taken in the arrangement of the tables to make interpolation easy and to ensure the maximum convenience in use, also fails to mention another very valuable feature—the little treatise on numerical differentiation and differential equations, which comes near the end. There is also a great deal of really valuable information in the introduction, and a very helpful bibliography of larger tables at the end.

In volume two, the 6- and 8-figure logarithms have been mentioned. There is also a table of antilogarithms, a function for which tables to more than four figures have been remarkably scarce up to the present. Naturally, too, there are tables of the logarithms of trigonometric functions, which, as in volume 1, are given for angles expressed in degrees and minutes, or in degrees and decimals, or in radians. The S and T functions are also given for all these arguments and for seconds of time as well. There are tables of $\log \Gamma(x)$ and of the logarithms of the hyperbolic functions.

Taking the two volumes together, it seems reasonable to suppose that they will suffice for the everyday needs of most workers who have calculations to do, though each will supplement them with tables for his own special work; perhaps he will want a selection of tables

for statisticians, or tables of Bessel functions, or maybe of factors. From this point of view the collection is not the successor to Chambers' Tables, but to such collections as those of Hoüel or Potin, Barlow, Hutton, Dale or Dwight. Certainly, with Barlow's tables on one side of the new book and Jahnke and Emde on the other, any worker would have a fine collection of tables at hand.

From a footnote to the preface, it appears that there is also an abridged edition of these 6-figure tables, in one volume, but the exact contents are not known to the reviewer. There is also a suggestion that the 64-page book of four-figure tables prepared by the same compiler for Messrs. Chambers is a miniature version of the present two volumes. It is certainly a very handy volume, but to the present writer it would have seemed that a nearer analogue is *Standard Mathematical Tables* by Milne-Thomson and Comrie.

J. H. A.

Five-Figure Tables of Mathematical Functions, by J. B. DALE. Second Edition. Pp. viii+121. (London: Edward Arnold & Co., 1949). Price 6*s*.

The first edition of this book must be familiar to most readers of this review. Since 1903 it has been one of the few convenient single-volume sets of miscellaneous tables compiled with the physicist and applied mathematician in mind. In addition to logs, antilogs and trigonometrical functions, it contained Bessel functions, gamma functions, elliptic integrals and Legendre functions, which are all of value at times to the ordinary physicist.

In the present edition the contents have hardly been altered: the table of logarithms is somewhat improved and there is now a table of the logarithms of hyperbolic functions. The old edition gave logs for the range 1·00(0·01)9·99, and the new gives, in addition, 1·000(0·001)2·999, which is a definite improvement. In the old edition the amount to be added for the next figure of the argument was given in the way that is usual with four-figure logarithms—columns for 1, 2, . . . 9, based on the mean differences of the line, were given opposite the entries. In the new edition this plan is retained for the first table, but for the second the actual differences are to be used, and there is a proper table of proportional parts, but, unfortunately, it is not on the same page as the logs themselves.

The whole book has been re-set, with modern "heads and tails" type, instead of the old, uniform-height type, and on paper which is very pleasant to handle. J. H. A.

The Theory and Use of the Complex Variable, by S. L. GREEN. Second Edition. Pp. viii+136. (London: Sir Isaac Pitman and Sons Ltd., 1949). 12*s*. 6*d*

This excellent little book may not find the favour it deserves, among mathematicians at least, because of the lack of rigour. Among physicists this will be less of an impediment, although the fact that the basic ideas are introduced non-rigorously should have been emphasized. For many it is indeed a considerable advantage to know what a subject is about first, and then to consider it rigorously.

Complex numbers are introduced by means of the elementary theory of equations, it being *assumed* that they obey the ordinary laws of algebra. The Argand diagram, de Moivre's theorem, infinite series and the exponential, logarithmic, circular and hyperbolic functions are treated in chapters I, II and III.

Chapter IV is devoted to the consideration of functions of a complex variable. Oddly enough the Cauchy–Riemann equations are left unnamed in the text. A curvilinear integral is defined, but neither its existence nor its uniqueness are discussed. This is followed by Cauchy's theorem, Taylor and Laurent expansions and contour integration by means of the residues theorem. It is a little surprising to find the contour integral representations of a function and its nth derivative omitted.

Chapter V deals with conformal transformations, the important Schwarz–Christoffel transformation has a separate chapter. The last two chapters are devoted to applications in potential and alternating current theory.

The text is admirably written; and, for the student who does not expect rigour, it will form an excellent introduction to a branch of mathematics of considerable importance to physicists. H. H. H.

CONTENTS FOR SECTION B

	PAGE
Mr. J. HOLDEN. Multiple-Beam Interferometry: Intensity Distribution in the Reflected System	405
Dr F. D. STOTT. Optical Transmission of a Colloidal Solution in a Magnetic Field	418
Mr. B. MELTZER. Electron Flow in Curved Paths under Space-Charge Conditions	431
Mr. W. WEST. The Accuracy of Measurements by Rayleigh Disc	437
Mr. R. L. G. GILBERT. A Dynamic Gravimeter of Novel Design	445
Dr. C. DODD and Mr. HU PAK MI. Viscosity and Density in the Supercooled Liquid State	454
Letters to the Editor:	
Professor G. TORALDO DI FRANCIA. The Radiation Pattern of Retinal Receptors	461
Reviews of Books	463
Contents for Section A	467
Abstracts for Section A	467

ABSTRACTS FOR SECTION B

Multiple-Beam Interferometry: Intensity Distribution in the Reflected System, by J. HOLDEN.

ABSTRACT. The intensity distribution within the reflected fringe system from a multiple-beam interferometer employing silvered reflecting surfaces is discussed in its dependence upon the reflectivities and phase conditions at the reflecting surfaces. Using the Fizeau fringes of equal thickness localized on the zero order Feussner surface, the reflected intensity distribution is examined experimentally as the reflection coefficients of the interferometer surfaces vary between 4% and 90%. In the range of low reflectivities, when the silverings used showed marked colours, the changes in the reflected system lead to the measurement of a phase quantity related to the optical constants of the silver in the form of the thin film. Also in this range, the reflected fringes have a symmetrical form which is of use in the examination of sources of low intensity. In the range of high reflectivities, the conditions for the use of the reflected fringes in topographical investigation are discussed. The findings apply to fringes of equal chromatic order as well as to Fizeau fringes in reflection.

Optical Transmission of a Colloidal Solution in a Magnetic Field, by F. D. STOTT.

ABSTRACT. The change in optical transmission of a solution of colloidal graphite in a magnetic field has been measured as a function of a field strength and of concentration, and the results obtained compared with those to be expected from theory.

It is found that the experimental results agree closely with the hypothesis that the change in transmission is due to the change in projected area of the plate-like particles when these are aligned by the magnetic field.

By comparison of theoretical and experimental curves the particle volume is found. The rate of decay, after removal of the field, of the change in transmission produced by the field has also been measured.

An approximate theory is given to connect this rate with the diameter of the particles, and from this the size of the particles has been calculated. The dimensions so found agree satisfactorily with evidence from other sources.

Electron Flow in Curved Paths under Space-Charge Conditions, by B. MELTZER.

ABSTRACT. A general, synthetic method of obtaining rigorous solutions of steady electron flow subject to space-charge forces is presented. The solutions are not obtained for given boundary conditions, but the boundary conditions are deduced from the solutions. Two examples of such solutions, involving strongly curved two-dimensional electron trajectories, are given; the method is in principle capable of giving the solutions of all possible electron flow patterns in three dimensions except perhaps those involving intercrossing trajectories. It is suggested that the subject offers scope for applied mathematical research at least on the same scale as potential theory.

The Accuracy of Measurements by Rayleigh Disc, by W. WEST.

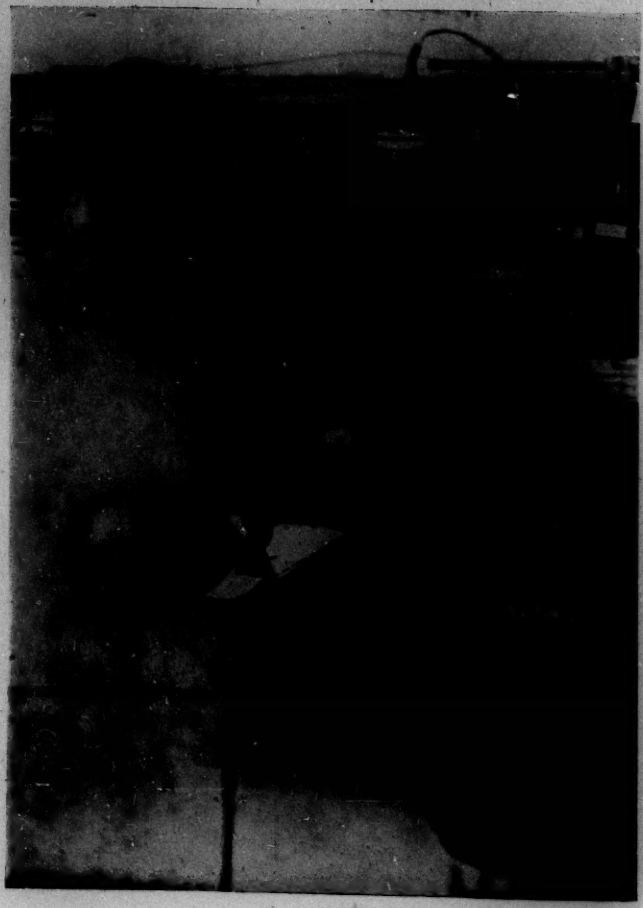
ABSTRACT. A review of proposals made for altering the formula due to König, on which are based measurements of air-particle velocity by Rayleigh disc, leads to the conclusion that there is insufficient evidence for altering the numerical constant in the formula. Comparisons between Rayleigh disc and other methods of calibration of individual microphones are discussed, and the possibility of difference due to reaction on the sound pressure by the vibration of the diaphragm is considered.

A Dynamic Gravimeter of Novel Design, by R. L. G. GILBERT.

ABSTRACT. A new type of gravimeter is described, which depends for its operation on the change of frequency of the natural vibration of a vertical wire stretched by a weight. The advantages of such an instrument are presented, and a description given of the design which has so far been evolved. The results of laboratory tests and of trials carried out at sea in H.M. Submarine *Talent* are given.

Viscosity and Density in the Supercooled Liquid State, by C. DODD and HU PAK MI.

ABSTRACT. In order to determine whether any structural change takes place when a liquid is supercooled, measurements have been made on the viscosity of pure phenyl ether, which by its melting point (26·85° c.) is suitable for accurate work. It has been found that in both the ordinary and the supercooled state the liquid obeys a formula of the type $\eta = A \exp(b/T)$, but that the value of b in the supercooled state, which was investigated down to 17° c. below the melting point, is significantly larger than the value of b for liquid above the melting point. It is shown that an accurate value for the melting point can be obtained from viscosity measurements without the liquid ever becoming solid. The temperature coefficient of density shows no detectable change in passing through the melting point.



PROFESSOR G. I. FINCH, M.B.E., D.Sc., F.R.S.,
President of the Physical Society, 1947-1949.